PREPARATION AND CHARACTERISATION OF NANOCOMPOSITES OF BIOMASS AND MONTMORILLONITE CLAY FOR USE AS BIOFUELS

A DISSERTATION SUBMITTED TO THE

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BY

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Declaration

I declare that this dissertation, submitted to the University of Fort Hare in fulfillment of the requirements for the Master of Science in Chemistry degree, is my original work except where references are acknowledged. This dissertation or work contained in it has not been submitted to any other educational institution.

Signature ……………. Date……………7 August 2014………………..

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I give honour and praise to God the Almighty, for giving me the strength and health I needed throughout my work.

I am also grateful to my family for giving me love and support.

Dedication

To Nyenge, and LJ

Abstract

The aim of the study was to prepare composites of clay and biomass which burn longer than unmodified biomass. Montmorillonite clay was converted to mono-ionic clay by ion exchange with sodium using sodium chloride solution. The mono-ionic clay was organically modified with an organic surfactant, methyl triphenyl phosphonium bromide. Nanocomposites were then prepared by combining the modified forms of the clay with sawdust. The three forms of clay used for the formation of composites were unmodified montmorillonite, mono-ionic montmorillonite and organically modified montmorillonite. The solution blending method was used to make the nanocomposites. FT-IR and XRD analysis showed that organic surfactant increases the interlayer space of the clay since it is bulkier than the inorganic cations that are naturally present in the interlayer space of montmorillonite. The combination of clay and sawdust resulted in the formation of exfoliated nanocomposites as shown by the absence of peaks in the low 2 theta angle in the x-ray diffraction data of the nanocomposite. The nanocomposite which was made from sawdust and 1% organically modified clay showed the best results in terms of burning time and thermal stability, as well as giving a calorific value closest to unmodified sawdust and the least amount of residue.

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Abbreviations

MMT-montmorillonite

Na-MMT-sodium montmorillonite

MTPB-methyl triphenyl phosphonium bromide

TGA-thermogravimetric analysis

DTG-differential thermal analysis

XRD-X-Ray diffraction

FT-IR-Fourier transform infrared spectroscopy

CHAPTER 1

1. Introduction

1.1 General background

As the world continues to industrialise and its population grows, it is becoming increasingly necessary to find alternative sources of energy to those that are available currently. The big world economies are heavily reliant on fossil fuels, resulting in the depletion of such fuels at an increasingly fast rate since the industrial revolution. Environmental concerns have also led to the call for the development of alternative, environmentally-friendly fuels since fossil fuels are a major source of pollution, the chief driver of global warming (Kiarii 2010), the main source of toxic gases in the atmosphere and the major cause of acid rain (Sciencetech 2010). Fossil fuels release more carbon annually than that fixed by plants, resulting in an excess of the greenhouse gas, carbon dioxide in the atmosphere. This has been linked to climate change (Sciencetech 2010).

Recent developments have seen more attention given to renewable energy sources, namely water, wind, solar, geothermal and biomass. Biomass is an important renewable energy source because of its availability, renewability, environmentally-friendliness and adaptability to various kinds of diesel engines, homes and industrial plants (Field, Campbell and Lobell 2007). It has the potential to increase energy security in regions without or with little fossil fuel reserves, to increase supplies of liquid transportation fuel and to decrease the net emissions of carbon into the atmosphere per unit of energy delivered. It is hoped that the carbon dioxide released when biomass is burnt to produce energy is used up by plants growing in the fields and plantations (raw materials for biomass) effectively reducing the greenhouse effect.

Before the start of the industrial revolution, biomass energy was the world's most dominant energy source. It still accounts for 7% of the world's primary energy consumption, especially in the developing world (Field, Campbell and Lobell 2007). Energy from biomass, in the form of wood, is widely used for cooking and heating in Asia and Africa. It is also frequently used as a source of industrial heat, particularly in the forestry and paper industries. Many rural communities still do not have access to electricity or other forms of fuel, thus placing a huge strain on the few sources of firewood that remain (Hall 1999). In Africa, accessing firewood has become more challenging each passing year for most rural communities as a result of uncontrolled deforestation by earlier generations (Maguire 1992). In some communities, women and children walk more than 10km to collect firewood which is just enough for a day's cooking. Other sources of energy such as electricity and gas are virtually unavailable in such communities or simply unaffordable.

The most direct way of prolonging the current reserves of fossil fuels for future generations and reducing greenhouse gas emissions is by reducing the dependence on fossil fuels. One way of achieving this is to improve the efficiency of the biomass energy system. With appropriate technologies, burning compacted biomass energy pellets as a heat source is being investigated as a viable and environmentally friendly use of biomass energy. Nanotechnology has been suggested to improve the efficiency of burning biomass fuel (Field, Campbell and Lobell 2007). In this project, it is hoped that nanotechnology can be employed in energy development by using modified biomass derived from sawmill dust, which is otherwise regarded as waste. The idea is to convert such biomass to efficient fuel for heating and cooking. Wood is potentially one of the cheapest sources of energy, if managed efficiently. It is renewable and growing large plantations creates employment for local communities and helps to mop-up the carbon dioxide produced when it is burnt, thereby reducing the greenhouse effect. Sawmills churn out vast amounts of sawdust annually, some of which deposits on site as waste before it is destroyed by burning. Harnessing this sawdust waste into an energy source can greatly reduce the energy challenges that are faced in some developing countries of the world. There are technologies in some parts of Europe, Canada and the United States of America, where sawdust is compacted and shaped into pellets (di Giacomo and Taglieri 2009). If sawdust is first modified so that it burns longer, there will be a significant increase in its value as a heating and cooking energy source, which can supply homes and factories at relatively low energy cost all year round (Leszczynska, et al. 2007).

One practical way that the heating time of sawdust can be increased is by using fire retardation technologies. One of the most effective ways of retarding the rate at which a material burns is combining it with clay (Kandola 2001). If sawdust is made into pellets, there are even greater gains. The energy per unit mass is increased, the pellets are easier to transport and store and they can be adapted for use in many applications (Lehtikangas 2001).

1.3 Problem statement and hypothesis

Most people in the developing world still find it hard to access energy for domestic heating and cooking, due to high costs and unavailability. There is need to develop an alternative fuel that is readily available and affordable for heating and cooking. One way to solve this will be to find some means of extending the heating/burning time of cheap materials. Biomass has been used as a source of heating/burning therefore it will be ideal to develop low cost biomass-based sources of energy. In this project, it is hoped that sawdust will be modified into a low-cost source of energy by converting it into a nanocomposite material that can provide a relatively larger surface area than the unmodified sawdust material. The composite material is to be made from biomass and a nanoclay that has the capability of retarding heating/burning.

1.4 Aims and objectives

The major aim of this research was to prepare and characterise nanocomposites of clay (Montmorillonite) and wood (sawdust) which burn longer than normal wood

Other objectives of the study were:

- To prepare mono-ionic clay
- To modify clay by allowing chains of surfactant to be introduced in between layers of clay
- To form nanocomposites of unmodified and modified clay with sawdust and characterise the products formed
- To vary the proportions of wood and clay in order to prepare nanocomposites with various energy properties
- To evaluate the heating/burning capacities by determining the time taken to burn and the calorific values of the nanocomposites prepared.
- To undertake a preliminary evaluation of the nanocomposites as a suitable biofuel for domestic heating and cooking.

1.5 Delineation and delimitations of study

The study focused on one chosen surfactant which was used to modify clay before it was combined with sawdust. One type of clay was used, namely montmorillonite (MMT). The biomass material used was sawdust obtained from Melanie sawmill near the small rural town of Alice in South Africa. The major limitation of this study was that combining clay with biomass is not a widely researched area therefore references on this subject were limited.

1.6 Dissertation outline

The dissertation is arranged into 6 chapters. Chapter 1 introduces the study as well as outlines the aims and objectives of the study, while Chapter 2 deals with the literature review. Chapter 3 outlines the experimental procedures that were carried out in the laboratory. Chapter 4 discusses the characterisation of materials produced.. Chapter 5 deals with the flammability studies that were carried out as well the thermal analysis on the raw materials and products. Chapter 6 gives a summary of the entire study and recommendations arising from the results.

1.7 References

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CHAPTER 2

2. Literature review

Wood continues to be an interesting, reliable, convenient, cheap and accessible source of energy. Some inventors have come up with novel ways of trying to make wood to burn more energy-efficiently. One such way has seen the advent of pellets. Studies have found that compressing wood shavings, bark and other biomass materials has many advantages such as more energy per unit mass, adaptation to special energy-efficient stoves and fireplaces, as well as use in boilers and environmentally-friendly industries (Vinterbäck 2004). Pellets are much easier to store and transport since they can be commercially packaged. They also have lower moisture content when compared to normal wood, thus they are better heat energy sources (Lehtikangas 2000). Other inventors have found ways of suppressing flaming in wood used for structural purposes, by applying a range of chemicals to them, but there is no documentation on chemical modification of wood for use as fuel. However, there are a lot of studies that have been carried out on the modification of synthetic polymers, such as nylon so that they do not burn, or that they burn without giving flames. One such way is to combine the polymer with minute quantities of phyllosilicate clay, usually montmorillonite. (Kiliaris and Papaspyrides 2010) It was established that clay loadings of as little as one percentage point have vast influences on the physical properties of nylon and flame retardation without impacting negatively on its performance. (Gacitua, Ballerini and Zhang 2005) One such property that can be improved is the resistance to flaming. The nylon burns longer but there is no significant change in the total amount of heat that is produced, as illustrated in Figure 1 below.

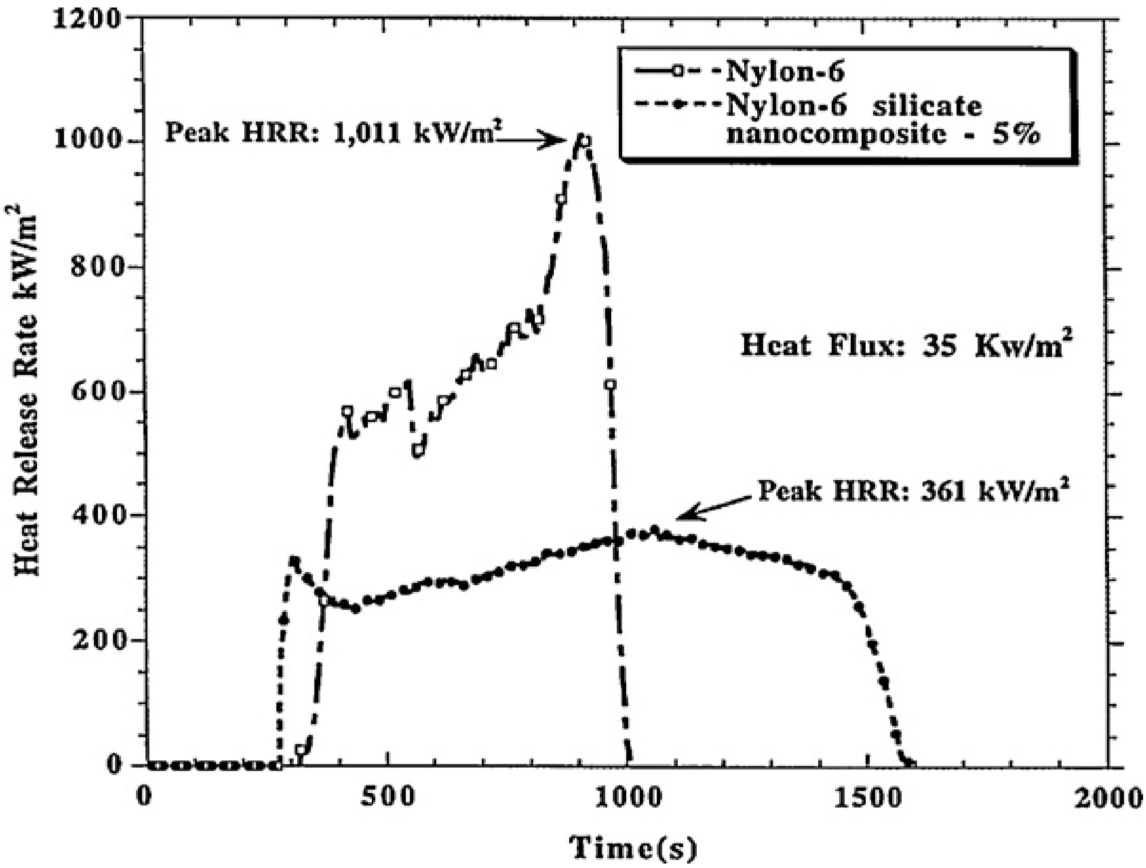

Figure 2.1 HRR plots of nylon-6 and nylon-6 nanocomposite **(Gilman, Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites, 1999)**

The modified nylon burns for a longer time than the unmodified nylon. Nylon-6 also has a higher peak heat release rate (HRR). Both samples however have the same calorific value. The modification thus reduces the peak heat release rate and elongates the burning time without significantly affecting the total amount of heat released.

This technology is to be applied to wood. If wood that has been combined with clay is made into pellets, the advantages of modification and pelleting can perhaps lead to the production of a reliable, cheap, accessible and efficient energy source.

2.1 Components of wood

Wood is a heterogeneous material composed of cellulose, hemicelluloses, lignin and other small amounts of organic and inorganic components. Cellulose is organised in fibrils and bundles, which are held together by hemicelluloses and the binder and encaser lignin. Figure 2 below shows a cross-section of these three main components of wood

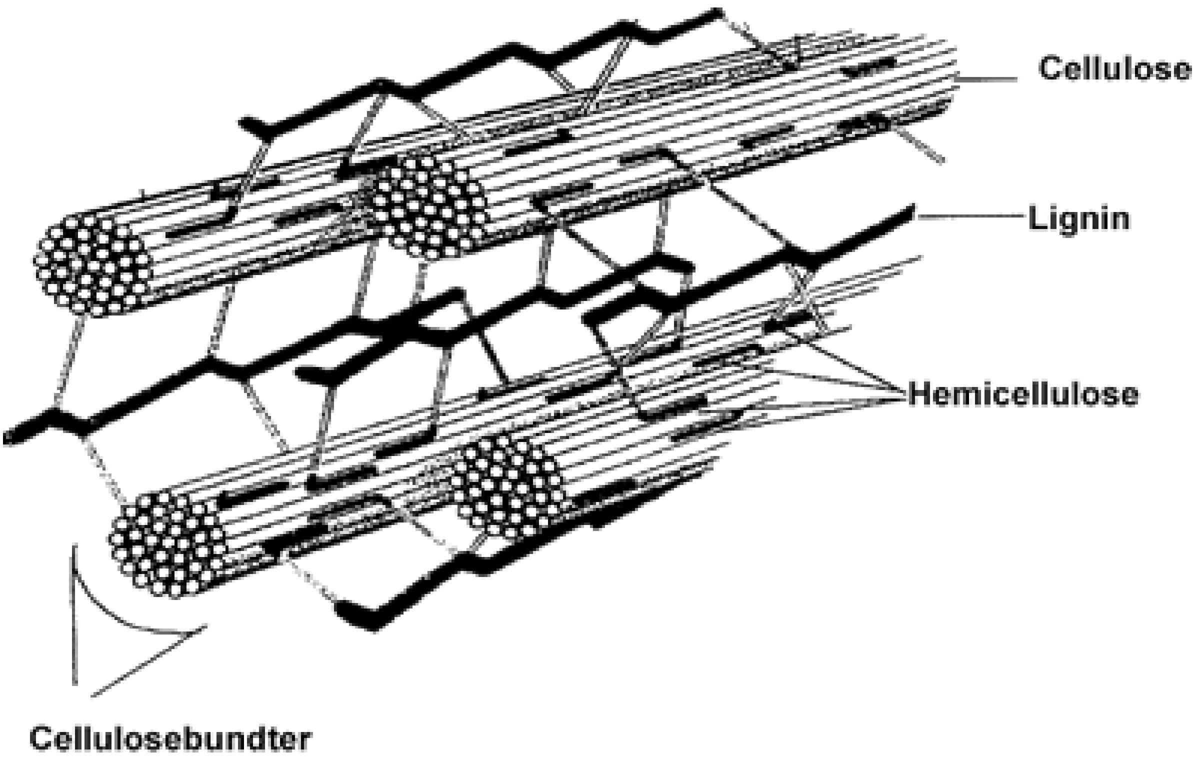

Figure 2.2 The three main components of wood (Rajai and Akira 2011)

2.1.1 Cellulose

The major component of wood is cellulose, which makes up to 60% of wood structure. Cellulose is a polymer of β-D-glucopyranose units linked by (1-4)-glycosidic linkages. The chair conformation of cellulose is illustrated in Figure 2.3. The degree of polymerisation in wood ranges between 8000-10000 monomer units. (Rajai and Akira 2011)

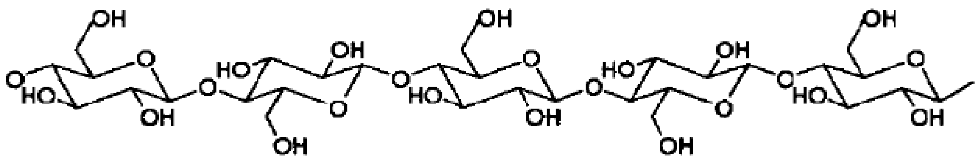

Figure 2.3: The chair conformation of cellulose (Apzilicta 2011)

Cellulose undergoes reactions typical of alcohols. It forms derivative of alcohols, such as esters and ethers. Strong hydrogen bonds between cellulose chains make it insoluble in common solvents. (Apzilicta 2011) In wood, cellulose forms part of a fibre-reinforced composite. The cellulose chain molecules, organised in fibrils, are held together and protected by hydrophobic lignin, which acts as a binder and encasement. The low cost of cellulose and the fact that it is a renewable resource, replenished by nature, results in it being widely used in medicine, technology and industrial manufacturing. Cellulose is an excellent combustible material and it is thus the main fuel source in wood. (Hon 2008)

2.1.2 Hemicellulose

Hemicellulose is a branched group of hetero-polysaccharides and the average degree of polymerisation is 200. Hemicellulose is mainly made up of: galactoglucomannans, arabinoglucuronoxylan, pectin, glucuronoxylan and glucomannan. The sugars which make up galactoglucomanns are: β-D-glucopyranose, β-D-mannopyranose and α-D-galactopyranose. Arabinoglucuronoxylan consists of 1-4-linked β-D-xylopyranose, partially substituted at carbon-2 by 4-0-methyl and α-D-glucuronic acid groups. It also contains 1.3 residues of α-Larabinofuranose per ten xylose units. Pectin is composed of D-galactogyluronic acid, D-galactose, L-arabinose and L-rhamnose residues. Glucuroxylan, which contributes approximately 30% of dry wood material, has a backbone made of (1-4)-linked β-D-xylopyranose units with about seven out of ten of the xylose residues containing O-acetyl groups at the carbon-2 and carbon-3 positions. One of the ten xylose units carries a (1-2) -linked 4-O-methyl-α-D-glucuronic acid group. Glucomannan contributes about 5% of dry wood mass. It is composed of β-D-glucopyranose and β-D-mannopyranose units linked by (1-4)-linkages (Connors 2008).

2.1.3 Lignin

Lignin is the third most abundant natural polymer after cellulose and hemicellulose. It is a major plant cell wall component which provides rigidity, internal support and transport of water and nutrients as well as providing protection against attack by microorganisms (Connors 2008). It is an armophous polymer consisting of phenyl propane units whose precursors are the aromatic alcohols: coumaryl, sinapyl and coniferyl alcohols. It is a highly irregular 3-dimensional chemically complex aromatic hetero-polymer of para-hydroxyphenyl propane units linked through many C-O-C and C-C bonds. Lignin is always associated with carbohydrates, in particular hemicelluloses, via covalent bonds. During thermal degradation of lignin, relatively weak bonds break at low temperatures, while cleavage of stronger bonds in the aromatic ring takes place at elevated temperatures (Connors 2008).

2.2 Chemistry of wood combustion

Wood is combustible and thermally degradable. When wood is exposed to sufficient heat, it decomposes or undergoes pyrolysis. This generates combustible gases which mix with oxygen to form an ignitable blend. For ignition to take place, there should be an external source of flame or spark, or the temperature should be high enough to cause auto-ignition, where the activation energy of the combustion reaction is attained (Babrauskas and Grayson 1992).

Exposure of wood to heat results in the release of substances that ignite and burn in the presence of oxygen. Ignition and combustion of wood is based on the pyrolysis of cellulose. The pyrolysis products react with each other and with gases present in air. Below, in Figure 2.4, is a summarised cycle of wood combustion.

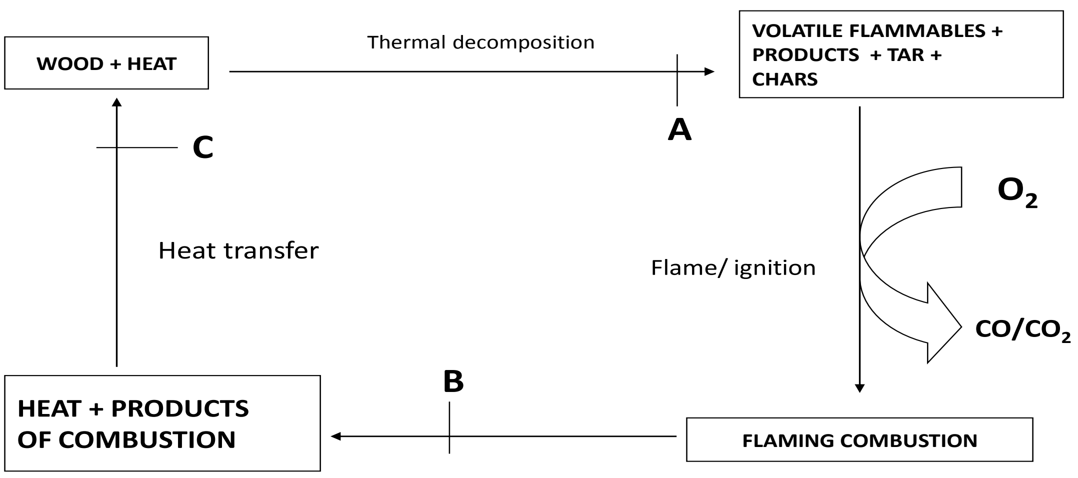

Figure 2.4 Summarized burning cycle (Apungu 2010)

When wood is ignited, temperature starts to rise leading to pyrolysis of cellulose as shown in the illustrated process. Some of the pyrolysis products are released as gases which then react with each other and oxygen thereby releasing a large amount of heat in process B. The heat produced further induces pyrolysis and combustion reactions. Pyrolysis of wood has two main pathways: the char forming pathway and the tar forming pathway. Formation of char serves as a thermal insulation barrier as well as a diffusion barrier for oxygen and volatile combustible components (Apungu 2010). If flame retardation is to be achieved, combustion in the char forming pathway should thus be induced. In the tar forming pathway, which is closely related to normal wood combustion and takes place at approximately 300 ^{o}C, pyrolysis produces high amounts of tar and levoglucosan which decompose easily into gases under the influence of heat. Thermal decomposition occurs in the char forming pathway where cellulose is firstly transformed into unstable cellulose that further decomposes into mainly carbon dioxide and water. When wood is ignited, the initial heat produced drives off the moisture in wood. Water is driven-off at 100 ^{o}C. When the temperature reaches 232 ^{o}C, gases such as carbon dioxide, carbon monoxide, acetic acid and formic acid are produced. Between 282 ^{o}C and 482 ^{o}C, a large amount of heat is produced as the gases burn. Large amounts of unburned combustible gases like methane, carbon dioxide, alcohols: such as methanol, more acids and water vapour are also produced at this stage. Secondary gases produced contain about 60% of the heat potential in wood. Their combustion, which takes place above 600 ^{o}C in sufficient oxygen, is important to achieve high overall combustion efficiency. When the gases have been burnt, the carbon chains of lignin and cellulose remain, smouldering and glowing (Apungu 2010). These burn for a longer time with a lower heat output when compared to the volatile combustible gases.

2.3 Flame retardants

A flame retardant is a compound or mixture of compounds which when incorporated into polymers, renders them less likely to ignite, or once ignited, less prone to burn effectively, whatever the extent of the effect. By definition, burning polymer nanocomposites can be therefore considered to be flame retarded, since the heat release rate (HRR) is significantly reduced relative to the pristine polymer, reflecting retardation of the flame spread in the case of developing fires (Schartel, Bartholmai and Knoll 2006). The "weakness" of this concept is, nevertheless, associated with the fact that the total heat evolved is scarcely influenced, indicating that no improvement of the polymer performance in fully developed fires. If the polymer is to be used as a fuel, then this "weakness" is actually an advantage.

Usually, fire retardants increase the dehydration reactions that occur during thermal degradation so that more char and less combustible volatiles are formed. The mechanism by which this happens solely depends on the particular fire retardant and the thermal-physical environment. The earliest wood fire retardants known to mankind were vinegar and alum, which were used by the ancient civilisations of Egypt and China. The Chinese also soaked wood in a solution of vinegar and alum with clay, thereby reducing and delaying fire spread. The Egyptians soaked reeds and grass used for roofing in seawater. The mineral salts which crystallised during drying acted as fire retardants. Developments in fire retardancy have relied on the introduction of aromatic rings into the polymer structure. This yields higher char residues. One of the most effective ways of protecting wood and lignocellulosic material from fire is by using reactive fire retardants based on bromine, for example SF_3Br, CH_2BrCl, CF_2BrCl and CF_2Br-CF_2Br, fluorine and chlorine compounds,. These halogen-based flame retardants interfere with the combustion cycle, primarily through free-radical scavenging mechanisms which inhibit flame propagation in the vapour phase. Specifically, they react with the polymer degradation radicals, as shown in the following reactions:

$HX + H\bullet \rightarrow X\bullet + H_2$ and

$HX + OH\bullet \rightarrow X\bullet + H_2O$, where X is a halogen

These reactions form less reactive species. X is typically chlorine, bromine, fluorine or iodine, with chlorine and bromine being the most commonly used (Skinner 1998). These compounds, however produce toxic substances and their use is being gradually phased out.

Structural wood can also be protected from fire with fire retardant intumescent coatings. On heating, these form a thick, porous carbonaceous layer which provides insulation against excessive increase in temperature and oxygen availability, thus preventing thermal decomposition. Additives such as phosphate salts and ammonium polyphosphate can also retard fires, although their solubility in water means they may be leached when exposed outdoors

Earlier studies on fire retardant treatments for wood started in the early 1930s in the Forest Products laboratory in the USA. Thousands of chemicals in various salts were evaluated for flame spread reduction, smoke and corrosivity. Most salts were found to be excellent as flame retardants,but promoted excessive smoke and glowing, corrosive to metals under some environmental conditions and were relatively expensive. These chemicals were mainly phosphorous-containing compounds, borax, zinc chloride and alkoxy silanes.

Inorganic fillers, such as metal hydroxides can also be used as smoke reducing non-toxic flame retardants. However, their efficiency is very low and a high concentration of filler material of up to 60% by mass is required to achieve significant flame retardancy. Nanofillers such as magnesium hydroxide are also being used, although their dispersion into wood material poses a significantly big challenge. The present emphasis is on developing cheap, environmentally-friendly fire retardants, with hydrophobic character, such as organoclays. Fire retardant polymer-clay nanocomposites are being developed in the textile and plastics industries. These have the advantage of not generating toxic gases, not imparting discolouration and having no negative effect on the mechanical strength of the polymer.

2.3.1 The effect of layered silicates on polymer combustion

The clearest evidence for the fire resistant character of polymer layered silicate nanocomposites (PLSN) has been obtained through cone calorimetry experiments. The presence of PLSNs causes the heat release rate (HRR) to quickly level off, resulting in a peak lower than the HRR curve of the neat polymer matrix. The primary parameter responsible for this lower HRR of the nanocomposites is the lower mass loss rate (MLR) which is reduced due to the development of a multilayered carbonaceous–silicate structure on the surface of nanocomposites during combustion. This structure is formed as a consequence of polymer ablation caused by pyrolysis, with the de-wetted clay particles left behind. Moreover, the montmorillonite layers reassemble to form stacks due to the degradation of the organic modifier, occurring at elevated temperatures, which renders silicates more hydrophilic and less compatible with the polymer matrix (Beyer 2002). The arrangement of silicates in an intercalated structure can be revealed via XRD examination on the chars produced. The carbonaceous char produced superficially during combustion is thus reinforced by silicates, creating an excellent physical barrier which protects the substrate from heat and oxygen, and slows down the escape of flammable volatiles generated during polymer degradation (Alexandre and Dubois 2000). This mechanism in which the HRR is reduced is universal for all types of nanocomposites, regardless of the nature of the matrix and the initial morphology (exfoliated or intercalated). This condensed phase decomposition process was further studied by Gilman (Gilman, Harris, et al. 2006), using a radiative gasification apparatus, shown in Figure 2.5.

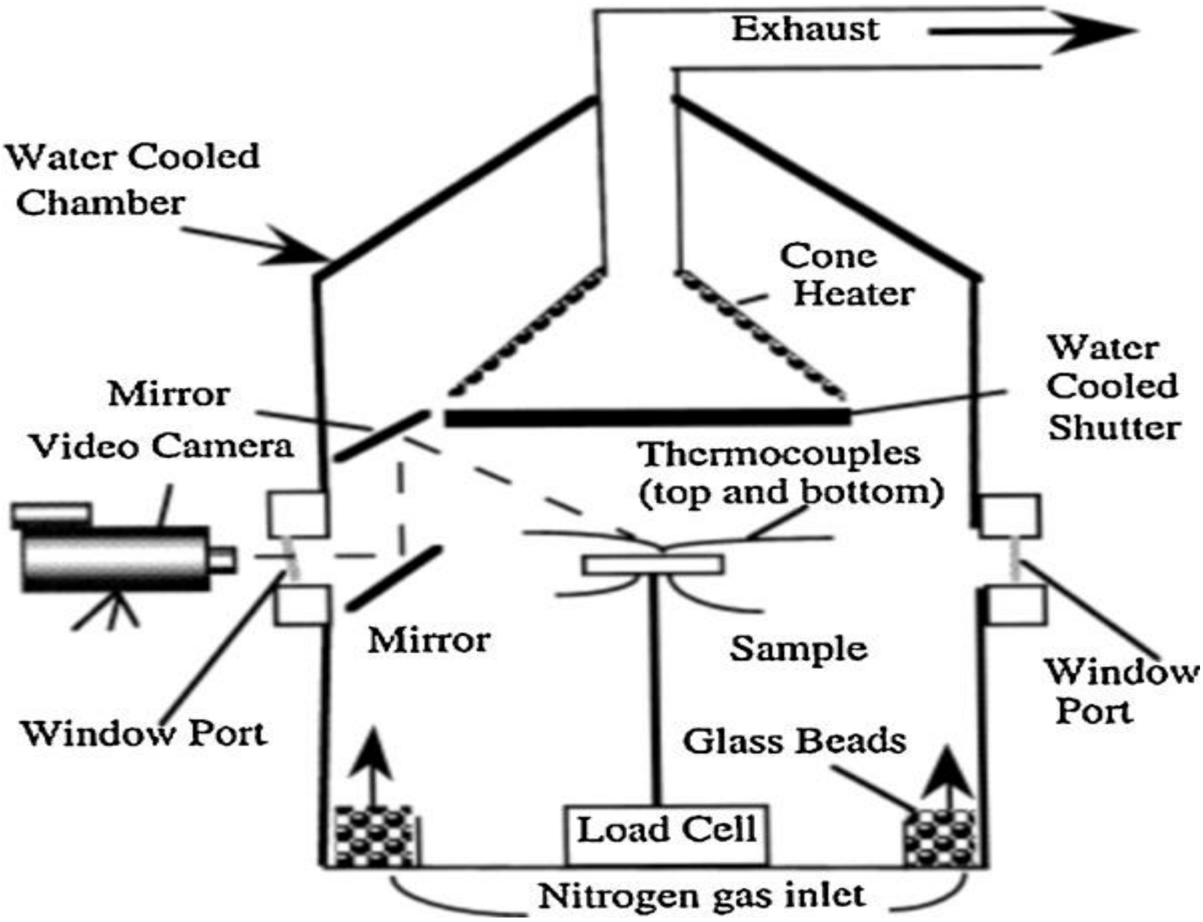

Figure 2.5. Schematic view of the radiative gasification apparatus (Gilman 1999)

Keeping the size of the samples and the external heat flux almost identical to that applied in the cone calorimeter, the experiments were performed in a nitrogen atmosphere in order to avoid any gas phase effects. It was revealed accordingly that, until char (of substantial thickness) was developed, the mass loss rates (MLR) of the nanocomposite and the virgin polymer were nearly the same, indicating that barrier formation controls flame retardancy.

Kashiwagi *et al.* (Kashiwagi, et al. 2004) showed that clay layers act as physical crosslinking sites among polymer chains, forming a network that restricts the mobility of macromolecules.

The effect becomes more pronounced with increasing clay loading and contributes additionally to the reduction of peak heat release rate (pHRR) by hindering the escape of decomposition products (Schartel, Potschke, et al. 2005). Clay particles are also reported to play a catalytic role in the promotion of char forming reactions. Studies on polyamide (PA6)/layered silicates nanocomposites conducted by Vaia and co-workers (Vaia, et al. 1999) have revealed increased carbonaceous char yields in the presence of silicates. The effect of clay has been verified even in polymers such as polyethylene (Zanetti, Bracco and Costa 2004) and polypropylene (Zanetti, Camino, et al. 2001) that do not normally exhibit char forming tendency. Char formation during polymer degradation is generally a complex process involving several steps which include conjugated double bond formation, cyclization, aromatization, fusion of aromatic rings, turbostratic char construction and graphitisation (Levchik and Wilkie 2000). Benson and Nogia (Benson and Nogia 1979) explained the oxidation chain reactions of organic molecules, by proposing the existence of two counteractive mechanisms. The first, occurring at low temperatures, causes chain scission with subsequent volatilization of the polymer via free-radical chain reactions, generating mainly hydroperoxides and oxygenated species. At higher temperatures, oxidative dehydrogenation becomes more probable and conjugated double bond sequences are formed, yielding thermally stable aromatized charred structures. Under ordinary burning conditions, the former mechanism predominates, while in the presence of silicates, enhanced aromatization accompanied by reduced rate of oxidation are observed, suggesting the prevalence of the second process (Zanetti, Camino and Thomann, et al. 2001). Hence the clay promotes the formation of (transient) char, which starts to degrade only at high temperatures. The intimate contact between silicates and polymer macromolecules is considered essential for the advance of charring process, as reflected by the performance of microcomposites in which volatilization is slightly delayed (barrier effect) but char generation does not occur (Bourbigot, Gilman and Wilkie 2004).

The catalytic effect of layered silicates on crosslinking or charring reactions derives mainly from the acid sites formed on silicates due to the degradation of organic treatment. The decomposition of alkylammonium salts proceeds, usually above 200°C, either via the Hoffmann elimination reaction (Figure 2.6) or via the SN_2 nucleophilic substitution reaction (Figure 2.7).

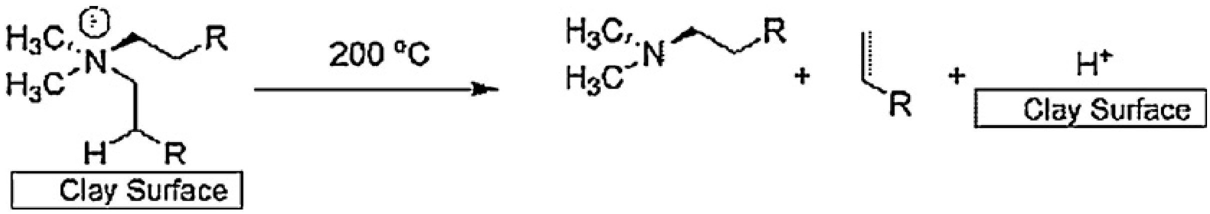

Figure 2.6 Hoffman elimination reaction of alkyl ammonium organic treatment (Morgan, Chu and Harris 2005)

$$RH_3N^+Cl^- \xrightarrow{\Delta} NH_3 + RCl$$

Figure 2.7 SN_2 nucleophilic substitution reaction of alkyl ammonium organic treatment (Bellucci, et al. 2007)

Hoffmann elimination occurs in the presence of a basic anion, such as hydroxide, which extracts hydrogen from the beta carbon of the alkyl group, yielding an alpha olefin and a free amine. Subsequently, the proton generated from the beta elimination reaction moves to the clay surface, upon which it forms a Bronsted acidic site (Song, et al. 2007). Once the organic modifier is decomposed completely, the amount of acidic sites will correspond to the cationic exchange capacity of MMT, which can be considered as acid activated clay, having direct interface with the remaining polymer. Clays in the acid form are well-known to facilitate hydrocarbon cracking and/or hydrocarbon aromatization, depending on the silicate structure and acidity (Vaccari 1999). Char formation is not only catalyzed by protonated silicates created after the decomposition of the organic modifier but it is also promoted by clay itself due to Bronsted and Lewis acid sites present on the clay lattice. Strongly acidic bridging hydroxyl groups and weakly acidic SiOH, residing at the layer edge, can act as Bronsted acid sites. Lewis acidity may arise either at the edge from partially coordinated metal atoms (such as Al^{3+}) or along the siloxane surface from isomorphic substitution of multivalent species (such as Fe^{2+} and Fe^{3+}) and crystallographic defect sites within the layer. When there is external heat flux, these acid sites can accept single electrons from donor molecules with low ionization potential, coordinate organic radicals or abstract electrons from vinyl monomers, leading to the crosslinking of polymer chains (Qin, et al. 2005).

Layered silicates also provide a confined, superheated environment in which the trapped decomposing polymer chains attain the opportunity to undergo additional degradation pathways for the benefit of flame retardancy (cage effect) (Jang, Costache and Wilkie 2005). Intermolecular reactions are favoured, leading to the formation of complex compounds. Thus, the volatilization rate is lowered for the formation of char, which is more likely to occur when aromatic rings and/or oxygen linkages are present in the polymer backbone (Van Krevelen 1979). The pHRR is not an ‘intrinsic’ polymer property such as the total heat released (THR), which conversely is not significantly influenced by the presence of silicates. THR is the most revealing aspect of a material’s performance in fully developed fires. The reduction in HRR with a small change in THR implies that clay fillers prolong the time of burning but decrease, negligibly, the total amount of material offered for combustion. (Schartel, Bartholmai and Knoll 2005).

Considering the above, the most important contribution of layered silicates to polymer's flame retardancy is the reduction in pHRR. The pathways that a burning polymer are believed to follow, are illustrated in Figure 2.8.

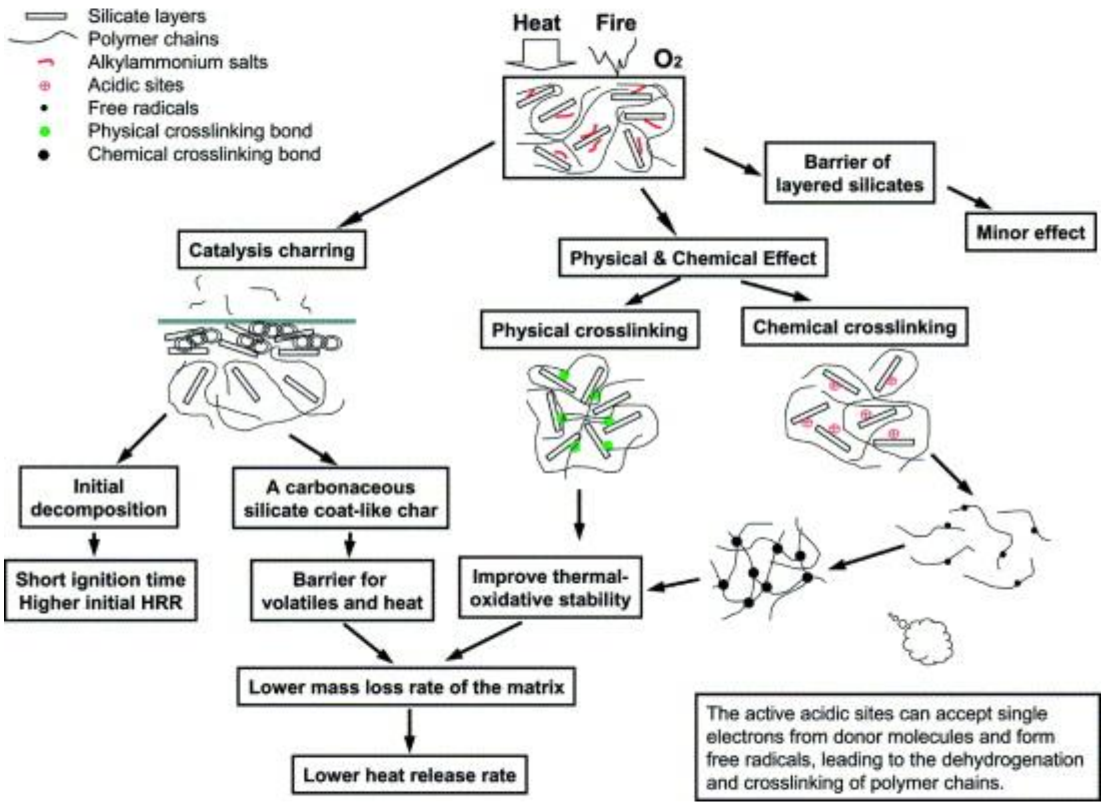

Figure 2.8: The Flame retardant mechanism of polymer/MMT nanocomposites. (Qin, Zhang, et al. 2005)

When a spark is introduced to a nanocomposite, a fire develops and there are several ways in which the silicates affect the burning process. The silicates can act as a barrier to volatiles which hinder the development of the fire. The silicates can also have a physical and chemical effect on the burning processes. This improves the thermal-oxidative stability which leads to a low mass loss rate of the matrix and low heat release rate. If catalysis charring occurs as the fire develops, there are two possibilities; initial decomposition leads to a short ignition time and a high release rate while the formation of a carbonaceous coat-like char forms a barrier to volatiles and heat, which leads to a low mass loss rate of the matrix and low heat release rate.

2.4 An overview on clay

Clay is made up of phyllosilicate minerals which include silicon and aluminium oxides, hydroxides and variable amounts of structural water. They exhibit several physiochemical properties like swelling, and ion exchange (Tzong-Yuan, et al. 2010). Natural clay is used, among other things, in making radioactive waste containers, in water pollutant removal and in industrial processes, such as paper making, chemical filtering and oil and gas drilling

2.4.1 Clay structure and chemistry

Clay is mainly composed of aluminosilicates. It has octahedral alumina and tetrahedral silica sheets organised in layers. The most common clay, montmorillonite (MMT), belongs to the smectite group of clays which is characterised by two tetrahedral silica sheets surrounding a central octahedral aluminium oxide sheet in a 2:1 ratio. The silicate layers are continuous and stacked one above the other with variable water layers between them. Amorphous substitutions in the octahedral and tetrahedral positions leave it with a net charge, satisfied externally by cations which are exchangeable. The cations are from natural earth metals such as sodium and lithium. Montmorillonite can exhibit two highly endothermic reactions which begin and reach maxima in the range 500^{o}C to 750^{o}C and 80^{o}C 0 to 900^{o}C. High temperature is required to rupture two types of hydroxyl bonds within the clay structure (Tzong-Yuan, et al. 2010). The first endothermic reaction results in loss of hydroxyl ions in the octahedral layer, leading to some loss in structural arrangement, which can be gained by rehydration. The hydroxyls in the silica sheets are lost during the high temperature endothermic reaction. The structure of montmorillonite clay is shown in Figure 2.9.

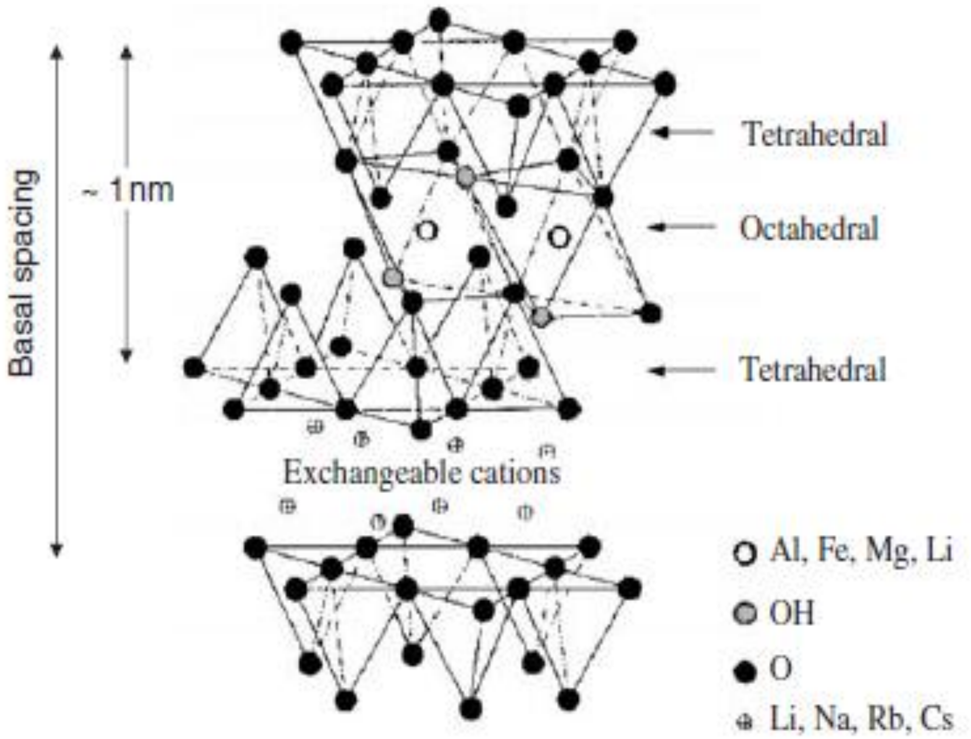

Figure 2.9: Structure of montmorillonite clay (Hussain, et al. 2006)

2.4.2 Modification to organoclay

Layered silicate clays are naturally hydrophilic, making them unsuitable for mixing and interacting with most polymer matrices, most of which are hydrophobic. Moreover, the stacks of clay platelets are held tightly together by electrostatic forces. An attempt to make a composite material using unmodified clay only, results in the clay being unable to interact with the matrix. However, intercalating with organic cations facilitates penetration of polymer molecules into the galleries, leading to the formation of a nanocomposite. Organically modified layered silicates, referred to as nanoclays, have increasingly become an attractive class of organic-inorganic hybrid materials because of their potential use in polymer nanocomposites, as adsorbents for toxic gases, as rheological modifiers in paints, inks, greases and cosmetics, in drug delivery carriers and effluent treatment (Pfaendner

2010). The term organoclay refers to smectites in which the interlayer inorganic cations, balancing the negative charge, are replaced by cationic organic surfactants. The surfactants used are quaternary ammonium or phosphonium halides with a long side chain, such as dodecylamine, cetyl trimethyl ammonium bromide or methyl triphenyl phosphonium bromide. The organic cations increase the interlayer spacing, as shown in Figure 2.10.

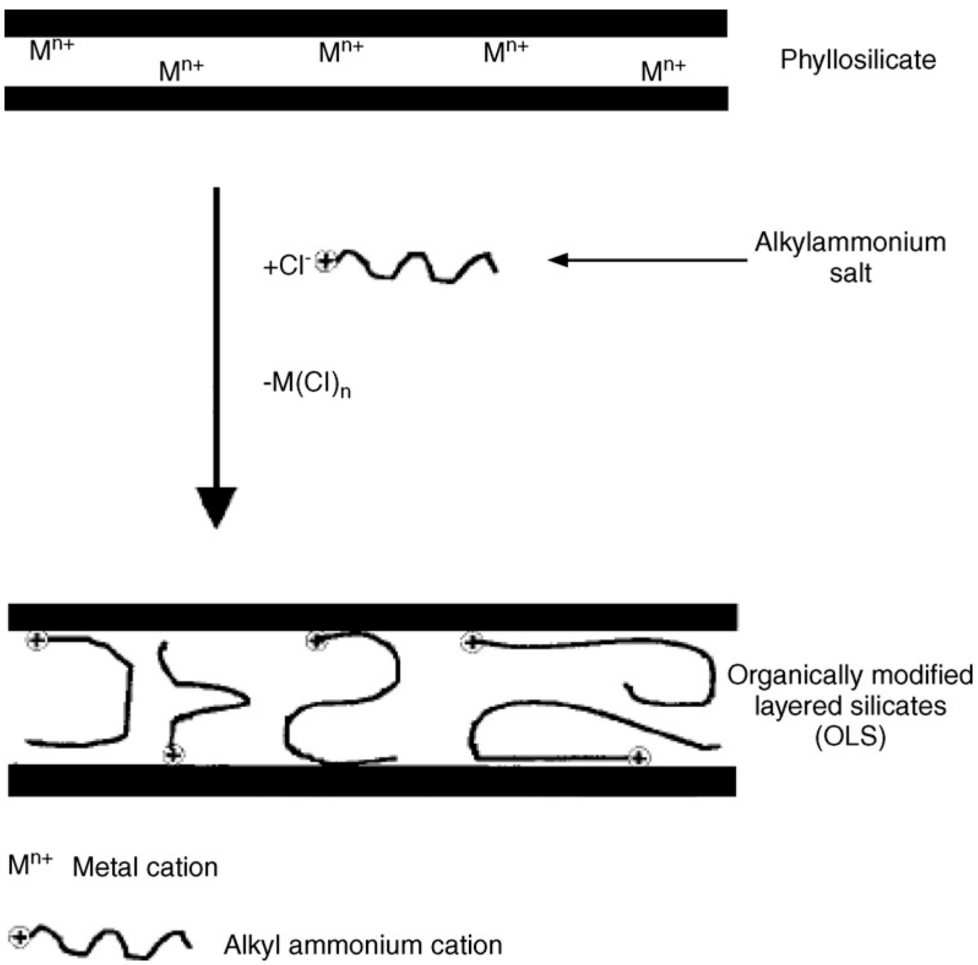

Figure 2.10 Illustration of clay organic modification (Zanetti, Lomakin and Camino 2000)

The clay can be modified by four methods, namely: ion exchange reactions, adsorption, edge-wise and in-situ synthesis. Ion exchange is the most commonly used method. The total number of replaceable small inorganic cations is governed by the moderate negative surface charge called the cation exchange capacity (CEC), which is the maximum number of exchangeable sites (Zayed, Oren and Mackay 1987). The organic cations reduce the surface energy and decrease the cohesive energy by expanding the interlayer space, thus facilitating wetting and intercalation of monomer units or polymers into the galleries, respectively.

2.5 An overview on nanocomposites and nanotechnology

Composites are a combination of two or more materials (reinforcing elements, fillers and composite matrix binder), differing in form or composition on a macro scale. The constituents retain their identities, that is, they do not dissolve or merge completely into one another although they may be miscible. Normally, the components can be physically identified and they exhibit an interface between one another (Metals 2011). The composite shows properties that were not present in the separate components. The properties of the composite are controlled by the behavior and properties of the interface.

Nanotechnology is a field of applied science whose theme is to control matter on the atomic and molecular scale, generally 100nm or smaller and the fabrication of devices of materials that lie within this size range (Nanoindustries 2012). It is a highly multidisciplinary field drawing from applied materials science, interface and colloid science, device physics, supra-molecular chemistry, chemical engineering and other fields. Nanocomposite materials are one, two or three dimensional materials made from distinctively different materials at the nanometer scale (Nanoindustries 2012). Polymer layered silicate nanocomposites exhibit immense enhanced properties and higher performance when compared to conventional polymer composites and pure polymers. Improvement of the material properties is obtained without an increase in polymer density.

2.5.1 Techniques used in nanocomposite synthesis

Three main methods are used to make polymer-clay nanocomposites. These are in-situ intercalative polymerization, melt interaction and intercalative solution polymerization.

2.5.1.1 Melt intercalation

In this method, the mixtures of polymer and clay silicate powder are heated above the polymer melt temperature. This makes the polymer achieve mobility allowing its chains to diffuse into the silicate clay galleries, producing an expanded polymer-silicate structure. This technique was used by Fornes and colleagues (Fornes, et al. 2001) in their evaluation of the effect of matrix molecular weight on nylon-6/clay nanocomposites. If the silicate layers are sufficiently compatible with the polymer, the polymer will enter the interlayer spaces of the silicate and form an intercalated or exfoliated nanocomposite (Chang, et al. 2003)

2.5.1.2 In-situ intercalative polymerisation

This method involves the use of organic treatments that have functional groups which the polymer monomer can interact with while polymerization begins at the treatment site. It relies on the swelling of the organoclay when monomer is added, followed by in-situ polymerization initiated thermally or by the addition of a suitable initiator. The chain growth in the clay galleries triggers clay exfoliation and nanocomposite formation (Rehab and Salahuddin 2005).

An example of in-situ polymerization is the use of surfactant monomers, such as 12-aminododecanoic acid (ADA) to link with nylon-6 polymer chains during polymerization, as illustrated in Figure 2.11.

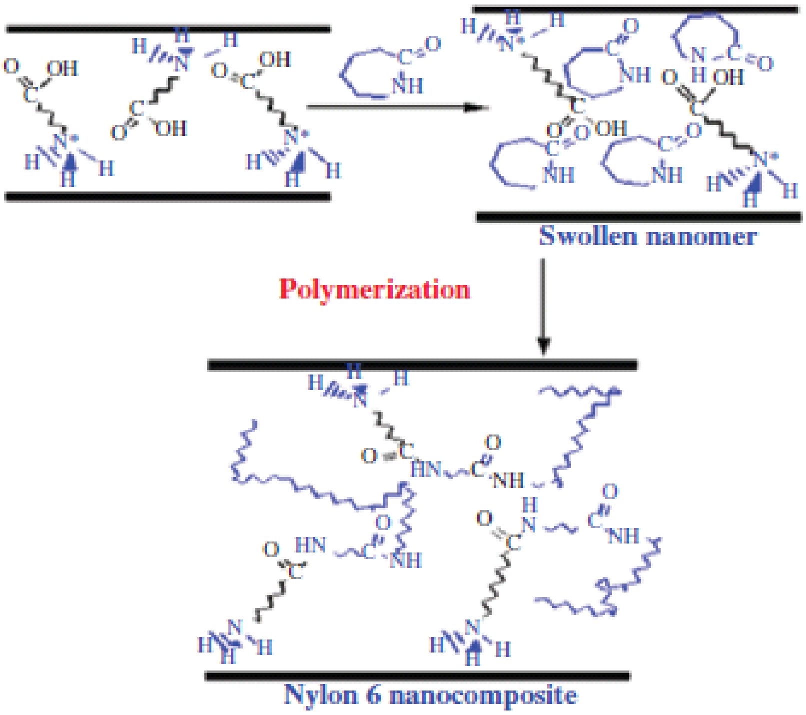

***Figure 2.11: Nylon 6 nanocomposite formed through in-situ polymerization with ADA-MMT* (Sczcenzsedy and Krkc 2010)**

2.5.1.3 Intercalative solution blending

This is the method that consistently yields exfoliated nanocomposite materials, subject to solvent, pre-treatment of clay and blending conditions (Beron, Wang and Pinnavia 2008). The solvent chosen should be able to dissolve the polymer material and sufficiently disperse the clay. The polymer is dissolved in a suitable solvent and mixed with the pre-treated clay. Having exfoliated nanocomposites allows the clay to be distributed in the polymer. (Hussain, et al. 2006).

Generally, the polymer is dispersed in clay in three main manners. These are phase separation, intercalation and exfoliation, as illustrated in Figure 2.12.

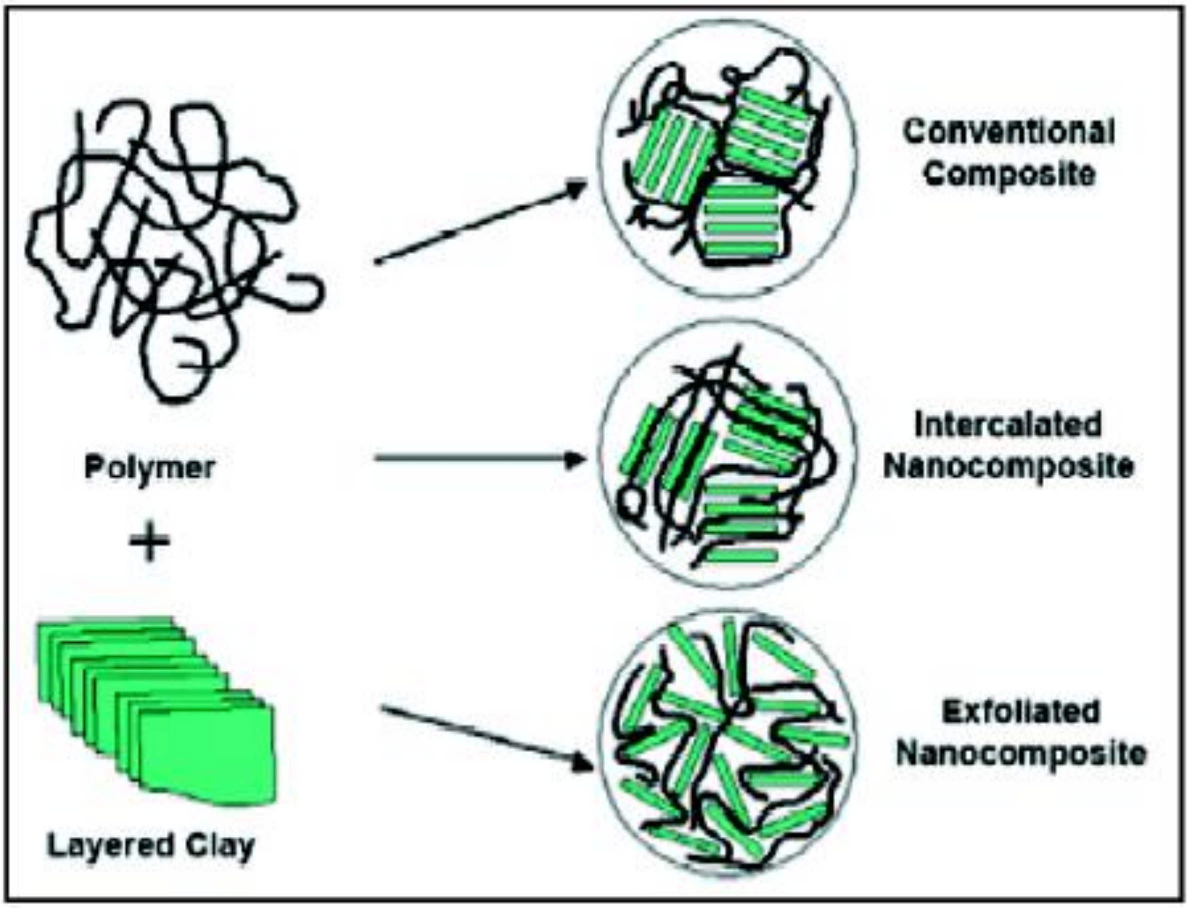

***Figure 2.12: Scheme of the three main types of layered silicates in polymers* (Denault and Labrecque 2004)**

In phase separated or conventional composites, the two materials maintain their structures with a minimum surface interaction. In intercalated nanocomposites, the polymer moves into the interlayer clay galleries. This increases the space between the clay layers. Exfoliated nanocomposites are usually the ones which exhibit the most enhanced performance when compared to the original materials on their own as well as the other type of nanocomposites. In exfoliated nanocomposites, the polymer penetrates the space between the clay layers and forces them apart. The clay loses its layered structure, thereby resulting in maximum surface interaction with the polymer.

2.6 Flammability tests

The three most widely used tests to characterize plastics flame retardancy are: the UL 94 vertical burning test, the limiting oxygen index (LOI) test and cone calorimetry. The UL 94 test, developed by Underwriters Laboratory Inc. (Laboratories 1997) is the most common procedure to check the regulatory compliance of a product, with respect to flammability. As shown in Figure 2.13, a specimen is mounted vertically so that the lower end is located above a cotton layer (to catch any flaming drip).

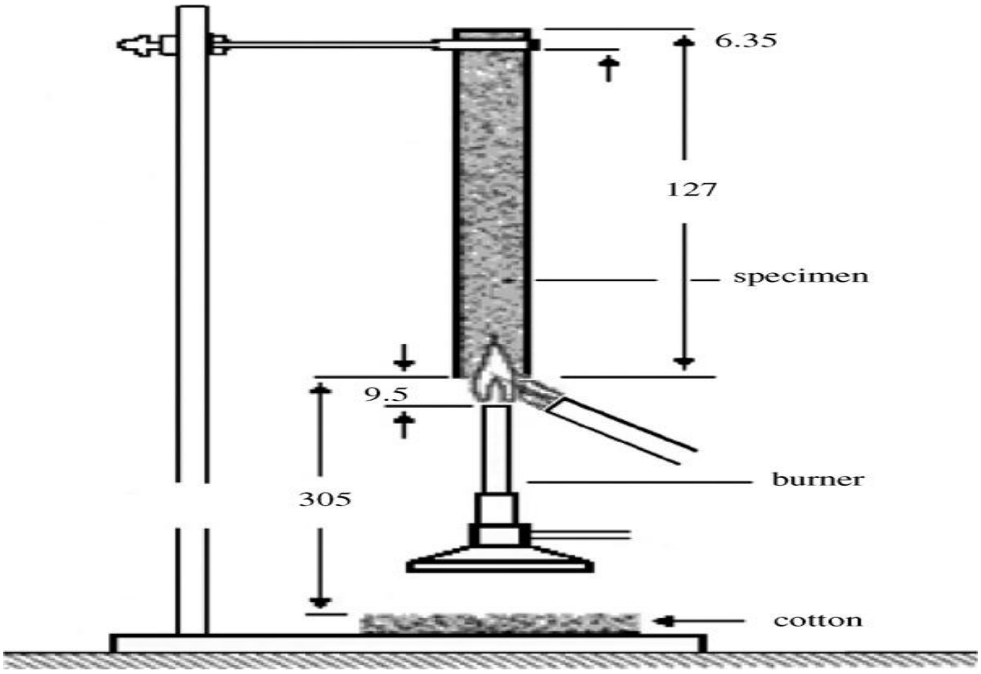

Figure 2.13: Schematic of the UL-94 vertical burning test **(Laboratories 1997)**

A flame is applied at the bottom of the specimen for 10 seconds, plus a subsequent application (10 s) if the specimen self-extinguishes. Two sets of five specimens are tested and the material is classified into three categories (V-0, V-1 and V-2) depending on its performance regarding the individual duration of burning for each specimen, the total burning time for all specimens and the presence or absence of burning drips. The specific burning characteristics required for each classification are summarized in Table 2.

Table 2.1: Classification categories in the UL94 flammability test (Lyon and Janssens 2005)

Classification	V-0	V-1	V-2
Total flaming combustion time for each specimen (s)	≤10 s	≤30 s	≥30 s
Total flaming combustion time for 3 specimens (s)	≤30 s	≤90 s	≥90 s
Flaming and glowing combustion time for each specimen after second flame application (s)	≤30 s	≤60 s	≥60 s

The LOI test, standardized as ASTMD2863 or ISO 4589, is applied to quantify a material's resistance to ignition. The apparatus consists of a glass tube in which the specimen is vertically mounted as shown in Figure 2.14

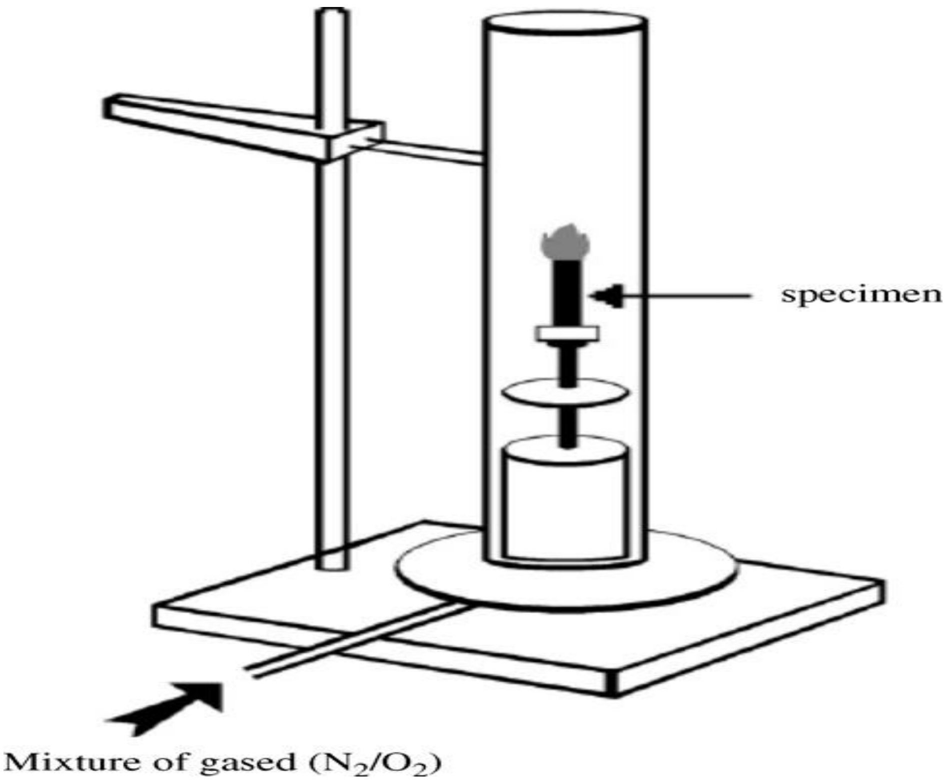

Figure 2.14: The LOI apparatus (Laoutid, et al. 2009).

During the test, a slow stream of oxygen/nitrogen mix is supplied at the bottom of the tube and a small candle-like flame is applied to the top of the specimen in an attempt to ignite it. The objective is to assess the minimum oxygen concentration in nitrogen that will support the combustion of the material for at least three minutes or for the consumption of 5cm of the sample. The more oxygen required (hence, the higher the LOI value), the better the material is considered to be flame retarded. Considering that air contains 21% oxygen, materials with a LOI value lower than 21 vol.% are categorized as combustible, while those with LOI above 21 vol.% are classified as self-extinguishing, since their combustion cannot be maintained at ambient temperature without the contribution of an external energy source (Wilkie 2005).

In a cone calorimeter (Figure 2.15), on the other hand, numerous fire properties, such as heat release rate (HRR), peak of heat release rate (pHRR), time to ignition (TTI), total heat released (THR), mass loss rate (MLR), peak of mass loss rate (pMLR) and specific extinction area (SEA), reflecting the smoke production of a material can be determined,.

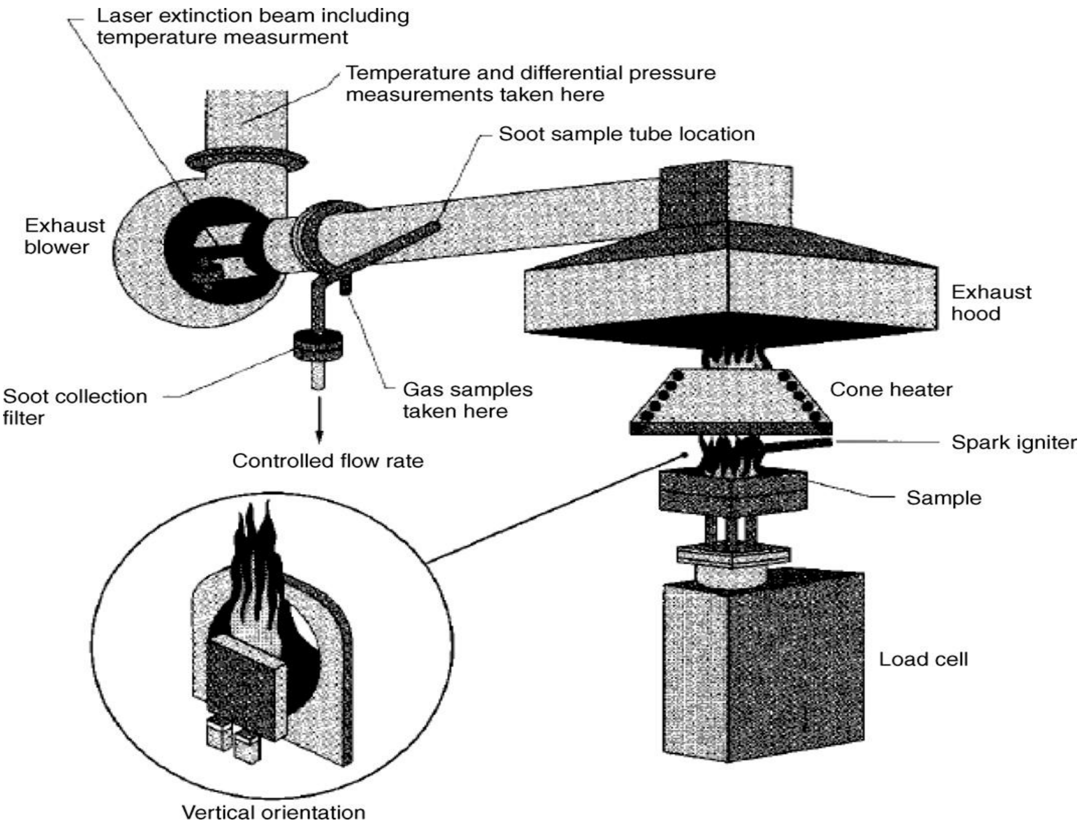

Figure 2.15: Schematic view of the cone calorimeter (Beyer 2002)

Among the data gathered, HRR and pHRR are the most important parameters needed to evaluate fire safety. HRR is thought to be the driving force of fire and pHRR represents the point in a fire where heat is apt to propagate further or ignite adjacent objects. The measuring principle of this test, standardized as ASTM E 1354 or ISO 5660, is that of oxygen consumption in the combustion gases of a specimen subjected to a defined heat flux. The gases produced are collected in an exhaust duct system with centrifugal fan and a hood and the HRR is calculated based on the fact that there is a constant relationship between the mass of oxygen consumed from the air and the amount of heat released throughout polymer combustion (Babrauskas and Peacock 1992).

2.7 Calorific values

The calorific value (CV) of a material is an expression of the energy content, or the heat value released when the material is burnt in air. The CV is usually measured in terms of the energy content per unit mass for solids; hence MJ/kg for solids, or volume MJ/L for liquids, or MJ/Nm^3 for gases (Pasthapodolous 2012). The CV of a fuel can be expressed in two forms, the gross CV (GCV), or the higher heating value (HHV) and the net CV (NCV), lower heating value (LHV). The HHV is the total energy content released when the fuel is burnt in air, including the latent heat contained in the water vapour and therefore represents the maximum amount of energy potentially recoverable from a given biomass source. The actual amount of energy recovered will vary with the conversion technology, as will the form of that energy, that is combustible gas, steam, or other sources. When quoting a CV, the moisture content needs to be stated, as this reduces the available energy from the biomass. It appears a normal practice to quote both the CV and crop yield on the basis of dry matter tonnes (dmt), which assumes zero percent moisture content. If any moisture is present, this reduces the CV proportionally to the moisture content.

2.8 Pellets

Pellets are fuel sources made from nearly any wood variety and produced by compressing the wood material in a hammer-mill in order to provide a uniform dough-like mass which is then shaped into pellets. The pelletizing process starts with dried sawdust being forced or pressed through holes in a rotating die. The pressure causes the temperature of the wood to increase greatly, briefly liquefying the lignins which act as glue and bind the pellets together. The lignin plasticises slightly, forming a natural "glue" that holds the pellet together as it cools. The extruded pellets are cut to length as they emerge from the die. The newly pressed pellets pass through a cooler in order to allow the lignin to harden. The pellets can be stored without risk of moulding or self-ignition and the energy content does not change during storage. The storage time is unlimited, but the refined fuel must be protected against rain (Vagonyte 2007). Modification of sawdust with clay followed by pelletising can be expected to provide a viable fuel source which lasts longer than firewood and currently pelletised wood combined. Figure 2.16 below shows a picture of pellets made from sawdust.

Figure 2.16: Swedish grade pellets made from sawdust (Vagonyte 2007)

Wood pellet production started in North America in the 1970s before spreading to Europe and other parts of the world. Today, wood pellets are produced and used on a global scale, although their use is still concentrated in developed countries (Bhattacharya 2002). Wood pellets have a major potential to replace fossil fuels for the production of heat and electricity (Nyström 2002). Traditional raw material assortments then need to be complemented with new ones. In some countries like Sweden, source-separated municipal and commercial waste is pelletised and used in large-scale systems for replacement of coal (Holm 2002). In Europe, Sweden, Denmark and Austria are forerunners in wood pellet use. In these countries, political decisions have promoted the increased use of bioenergy, a model which can also be followed by developing countries.

Pellet fuel, pellet appliances and also pellet logistics (Hahn 2002) are to an increasing degree, being tailored to fit national standards in Europe, but there is also work going on in order to establish international standards. In Sweden, new pellet production capacity is, to a high degree, integrated with district heating in order to improve the energy balance of the drying of wet raw materials (Mared 2002). Measures like this considerably influence the cost of fuel production (Thek and Obernberger 2004). Equipment for small-scale production of pellets such as the pellet stove and boiler shown in Figure 2.17 below are now available on the market,.

Figure 2.17: A pellet stove and pellet boiler (Vagonyte 2007)

Several critical aspects of combustion characteristics for wood pellets, such as emissions (Olsson and Kjällstrand 2004), (Ohlsson and Martorana 2002), (Eskilsson, Rönnbäck, et al. 2004), (Wiinikka and Gebart 2004), (Kja¨llstrand and Olsson 2004), (Obernberger and Thek 2002), (Lundberg 2002), slagging (Öhman, et al. 2004), (Öhman, Boman, et al. 2004), influence of physical and chemical fuel composition (Kjällstrand and Olsson 2004) as well as optimization of burner efficiency (Eskilsson, et al. 2004) have been examined. Researches on these and similar topics are still ongoing around the world.

In recent years densification has prompted significant interest in the developing countries as a technique for utilization of residues as an energy source (Bhattacharya 2002). Utilization of agricultural and forestry residues is often difficult due to their uneven characteristics. This drawback can be overcome by means of compaction of the residues into compounds of high density and regular shape. Densified biomass produced in developing countries is mostly in the form of briquettes, which are used directly to substitute fuel wood or for carbonizing to produce briquetted charcoal. The use of pellets in developing countries so far is still insignificantly small (Bhattacharya 2002). This shows that developing countries are lagging behind in this regard when considering that the turnover in the Swedish pellet industry was about 70 million Euros in 2001. Pellets produced in Sweden are mainly made of sawdust. (Du Rietz 2002). In order to establish a market for pellet heating systems, it is useful to support the ‘‘supply side’’ (pellets and boiler suppliers) and the ‘‘demand side’’ (building owners). Pellets as a package for bio-energy are easy to distribute and store. The most important thing is to make their price competitive when compared to fossil fuels. In Sweden, the pellet production capacity expanded during the 1990s to around one million tonnes per year. The fuel is still mostly delivered to large boilers converted from coal. The fast expansion of the large-scale market also paved the way for an expansion of the midsize and the private home market, a market that in 2001 expanded by around 100%. This expansion may continue for many years. The next milestones are to establish a quality standard for pellet fuel; standardization is now being extended in international co-operation, and the development of quality certification for pellet burners and stoves (Dahlstro¨m 2002). In Africa, the challenge is to develop the pellet industry from almost nothing, starting with harnessing the sources, the production of the pellets themselves, their distribution and use in industries and domestic units. There are stoves on the continent which use twigs and these could be adapted easily to use pellets.

Table 2.2: A summary of the advantages and disadvantages of pellets (Vagonyte 2007)

General advantages	Pellet advantages for domestic use	Disadvantages
Reduces dependence on oil, gas and electricity	More convenient to store than any other type of wood as it doesn't degrade due to low moisture content (less than 10%).	Pelletizing process requires a certain amount of energy input and may result in a higher price compared to wood logs, briquettes or other forms of wood.
Sustainable source of fuel: Wood pellets are a clean, environmentally friendly, natural, renewable and fuel resource	High energy value and, therefore, cost effective product: one ton of wood pellets has the heat value of more than one and a half tons of wood and stacks easily in one third the space. This makes it possible to easily store fuel for the entire season	In comparison with oil, there is a need for a larger storage facilities, regular control and removal of ashes
Pellet fuel cost is not dictated by world events; therefore cost is more affordable and predictable	Requires less maintenance: heating process is automatic. Only minimal clearance (mainly removal of ash) is needed for appliance installation (due to the near total combustion	
Provides employment opportunities as it is a native fuel	(around 98.5%) pellet stoves produce virtually no creosote. This also allows installation of a pellet stove by direct vent without a chimney	
Less ash and emissions-since pellet stove emissions are so low, they can be burned in most areas even those with burning restrictions	Cost-efficient: high energy efficiency (due to a low moisture content) which results in a reduced cost	
	Easier to handle - easiest fuel to transport and feed into burners–pellets are blown with a special pump from a truck to the storage room and are used in automatic machinery. When compared to wood or other types of wood, less volume to transport and store (due to higher energy density)	
	Air quality - clean, CO_2 -neutral pellet fuel enhances the air quality by substituting wood log burners, reducing fine dust emissions. Pellets have been proven to provide the cleanest combustion of any solid fuel	
	Standard technical characteristics and low moisture content – burns predictably and provides a consistent heat output	
	Furthermore, they have around 10% moisture content, considerably less than the 25 to 55% typical of chips, so that less energy is wasted boiling off water	
	Easy to ignite due to a consistent size and low moisture content	

2.10 Characterisations

Cone calorimetry, thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR) and X-Ray Diffraction (XRD) were used to determine the characteristics of the nanocomposites prepared and the starting materials.

2.10.1 Cone calorimetry

This is used to measure parameters such as: calorific value, char residue, time to ignition, heat release rate, time to peak heat release rate and smoke production. These parameters describe flammability and smoke emission behaviour of the wood-clay nanocomposite (Beyer 2002). In this project, the type of calorimeter that was available, however, only measures calorific values.

2.10.2 Thermogravimetric analysis

TGA was employed to determine the thermal properties, oxidation temperature and ash content. The sample was loaded onto a pan which was placed on a balance. A furnace then encloses the sample and the temperature can be increased at different rates in different environments. The constituents of the sample burn-off at different rates, thus the weight percentages of the constituents can be determined (Price, et al. 2006).

Thermogravimetric analysis measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used to primarily determine the composition of material and to predict their thermal stability at temperatures of up to 1000 °C. The technique can characterise materials that exhibit weight loss or gain due to decomposition, oxidation or dehydration. Changes in weight result from physical and chemical bonds which form and break at elevated temperatures. These processes may evolve volatile substances or form reaction products that result in change of weight.

In TGA, the weight of a sample is continuously recorded as the temperature is increased. Samples are placed in a crucible that is positioned in a furnace on a quartz beam attached to an automatic recording balance. The horizontal quartz beam is maintained in the null position by the current flowing through the transducer coil of an electromagnetic balance. A pair of photosensitive diodes acts as a position sensor to determine the movement of the beam. Any change in the weight of the sample causes a deflection of the beam, which is sensed by one of the photodiodes. The beam is then restored to the original null position by a feedback current sent from the photodiodes to the coil of the balance. The feedback current is proportional to the change in weight of the sample (Willard, et al. 1988).

2.10.3 Differential thermal analysis

Differential thermogravimetric analysis (DTG) is a technique in which the rate of material weight changes, on heating versus temperature, are plotted. This is usually used to simplify the reading of weight versus-temperature thermogram peaks that occur close together.

2.10.4 Infrared spectroscopy

This was used to analyse the chemical nature of the nanocomposites and the raw materials. Fourier transform infra-red (FTIR) technique is based on the excitation of molecular vibrations by light absorption. It is widely used in the determination of structure and identification of organic and inorganic compounds. It is mainly used in the identification of functional groups present in a given sample.

In infrared spectroscopy, infrared radiation is passed through a sample. Some of the infrared radiations are absorbed by the sample and some pass through (transmit) the sample. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures produce the same infrared spectrum. This makes FTIR spectroscopy useful for several types of analyses, including: identification of an unknown material, quality control of samples and the determination of the amounts of components in a mixture. The size of the peaks in the spectrum is a direct indication of the amount of material present.

The sample analysis process entails the emission of infrared radiation from a black body source. The beam of radiation passes through an aperture which controls the amount of energy presented to the sample (and ultimately to the detector). The beam enters the interferometer where the 'spectral encoding' takes place. The resulting interferogram signal then exits the interferometer. The beam enters the sample compartment where it is transmitted through or reflected off the surface of the sample, depending on the type of analysis being carried out. This is where specific frequencies of energy, which is uniquely characteristic of the sample, are absorbed. The beam finally passes through to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal.

2.9.5 X-Ray Diffraction Analysis

XRD was used to probe the crystal lattice structure of the nanocomposites and clay. The clay is characterised by a diffraction angle. An increase in the space between the clay layers results in the Bragg's angle peaks of the 2θ being shifted to lower values in accordance with Bragg's law. Lower 2θ values are expected after modification to organoclay since the organic surfactants increase the clay interlayer d-spacing. Formation of exfoliated nanocomposites results in no peak being detected (Okamoto 2005).

X-rays are diffracted from the planes of a crystal (diffraction analysis). This method depends on the wave character of the X-rays and the regular d-spacing of the planes in a crystal. Although diffraction methods are normally used for quantitative analysis, they are most widely used for qualitative identification of crystalline phases. X-ray powder diffraction analysis is a powerful method by which X-rays of a known wavelength are passed through a sample to be identified in order to identify the crystal structure. X-ray diffraction techniques are based on the elastic scattering of X-rays from structures that have long-range order. The wave nature of the X-rays means that they are diffracted by the lattice of the crystal to give a unique pattern of peaks of 'reflections' at differing angles and of different intensity, just as light can be diffracted by a grating of suitably spaced lines. The diffracted beams from atoms in successive planes cancel unless they are in phase, and the condition for this is given by the Bragg relationship:

$$n\lambda = 2dSin\theta$$

Where, λ is the wavelength of the X-rays, d is the distance between different planes of atoms in the crystal lattice; θ is the angle of diffraction. The X-ray detector moves around the sample and measures the intensity of these peaks and the position of their position [diffraction angle 2θ]. The highest peak is defined as the 100% peak and the intensity of all the other peaks are measured as a percentage of the 100% peak

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CHAPTER 3

3. Experimental procedures

Experimental procedures involved purifying montmorillonite clay, converting it to the mono-ionic form by replacing the several interlayer cations with Na^+, converting the mono-ionic clay to organoclay and preparation of nanocomposites of various forms of the montmorillonite clay and sawdust, using a solution blending method with zinc chloride as the solvent. Montmorillonite clay was sourced from Melanie Sawmill, which is near the rural town of Alice in South Africa. The sawdust was sieved using a 710µm sieve. The various raw materials and the products prepared were analysed using FT-IR spectroscopy, X-Ray Diffraction (XRD), thermogravimetric analysis and cone calorimetry.

3.1 Materials

Montmorillonite nanoclay from BaoBio Holdings (Pty) Ltd was used as the nano-component of the nanocomposites, while sawdust from Melanie Sawmill near the town of Alice, was the ignitable biomass component. Methyl triphenyl phosphonium bromide, purchased from Aldrich Chemicals, was used to organically modify the montmorillonite. Sodium chloride (99.5%) from MET-U-ED CC was used to prepare mono-ionic montmorillonite by ion exchange. Silver nitrate, from Saarchem, was used in the detection of chloride ions washed away after ion exchange. Zinc chloride, from Saarchem, was used to prepare the solvent used in the solution blending method.

3.2 Preparation of mono-ionic montmorillonite clay

Montmorillonite (15g) was measured into a 500mL conical flask and 200mL of 1M sodium chloride solution was added. The flask was placed on a rotary shaker for 12 hours at a speed of 163 revolutions per minute (rpm). After 12 hours, the contents of the flask were allowed to settle and excess sodium chloride supernatant solution was carefully decanted. Another 200mL of sodium chloride solution was added and the shaking process repeated for another 12 hours in order to ensure maximum ion exchange. After settling and decanting excess supernatant, the clay residue was washed with de-ionised water five times in order to remove chloride ions. (Triantafillidis *et al,* 2002).In order to aid settling of the clay after each wash, the slurry was centrifuged for 15 minutes and the supernatant decanted off. In order to detect whether chloride ions were still present at the end of the washing process, a few millimetres of the solution were mixed with a few drops of silver nitrate solution.

$$Ag^{+}(aq)\ Cl^{+}(aq) \longrightarrow AgCl(s)$$

The presence of chloride ions was detected by the appearance of a white precipitate due to the formation of silver chloride. After making sure there were no chloride ions, the slurry was then dried at 120 ^{o}C in an oven.

3.3 Preparation of organically modified montmorillonite

Mono-ionic montmorillonite (6g) was suspended in 300 mL of hot deionised water in a conical flask and 2.3g of the organic surfactant methyl triphenyl phosphonium bromide (MTPB) was added to 120 mL of deionised water in a separate conical flask and stirred for 5 minutes. The contents of the two conical flasks were then mixed and placed on a hot plate with a magnetic stirrer. The temperature of the mixture was maintained at 75 ^{o}C for 2 hours. The product was then filtered and washed with deionised water until no bromide ions were detected with 0.1M silver nitrate solution. The product obtained was dried in an oven at 60 ^{o}C for 12 hours.

3.4 Preparation of nanocomposites of sawdust and unmodified montmorillonite

Composites were prepared with various loadings of unmodified clay using the solution blending method. The solvent used was saturated zinc chloride and the nanosized component used was montmorillonite clay. The sawdust was first sieved through a 710 µm sieve.

3.4.1 Preparation of nanocomposite with 1% clay loading

Montmorillonite clay (0.0300g) was dispersed in 60 mL of saturated aqueous zinc chloride in a 250 mL conical flask solution and stirred for 1 hour at room temperature. Sawdust (3g) was added and rapidly stirred for 1 hour at room temperature. The mixture was transferred into a 250 mL 3-necked round-bottomed flask and heated for 3 hours at 98 ^{o}C. The mixture was then allowed to cool before it was filtered and washed with deionised water and dried in an oven for 1 hour at 80 ^{o}C. Other clay loadings reported in Table 3.1 were also prepared similarly, as reported here in Section 3.4.1.

Table 3.1: Amounts of montmorillonite and sawdust that there combined in the nanocomposites

	Montmorillonite/g	Sawdust/g
1% clay loading	0.03	3.00
5% clay loading	0.15	3.00
10% clay loading	0.30	3.00

3.5 Preparation of nanocomposites of sawdust and mono-ionic montmorillonite

In this procedure, composites were prepared with varying loadings of montmorillonite clay which had been modified with sodium chloride. The solvent used was saturated zinc chloride and the nanosized component was mono-ionic montmorillonite clay.

3.5.1 Preparation of nanocomposite with 1% mono-ionic clay loading

Mono-ionic montmorillonite clay (0.0300g) was dispersed in 60 mL of saturated aqueous zinc chloride solution and stirred for 1 hour at room temperature in a 250 mL conical flask. Sawdust (3.0000g) was added and rapidly stirred for 1 hour at room temperature. The mixture was transferred to a 250 mL 3-necked round-bottomed flask and heated for 3 hours at 98 ^{o}C. The mixture was then allowed to cool before being filtered and washed with deionised water and dried in an oven for 1 hour at 80 ^{o}C. Different amounts of clay loadings were also used as reported in Table 3.2, using the same procedure.

Table 3.2: Amounts of mono-ionic clay and sawdust that were used to prepare the nanocomposites

	Mono-ionic clay/ g	Sawdust/ g
1% clay loading	0.03	3.00
5% clay loading	0.15	3.00
10% clay loading	0.30	3.00

3.6 Preparation of nanocomposites of sawdust and organically modified clay

In this procedure, composites were prepared with varying loadings of montmorillonite clay which had been modified with sodium chloride, followed by methyl triphenyl phosphonium bromide. The solvent used was saturated zinc chloride and the nanosized component used was MTPB-montmorillonite clay.

3.6.1 Preparation of nanocomposite with 1% organically modified clay loading

Organically modified montmorillonite clay (0.0300g) was dispersed in 60 mL of saturated aqueous zinc chloride solution in a 250 mL conical flask and stirred for 1 hour at room temperature. Sawdust (3.0000g) was added and rapidly stirred for 1 hour before it was transferred into a 250 mL 3-necked round-bottomed flask and heated for 3 hours at 98 ^{o}C. The mixture was then allowed to cool before it was filtered and washed with deionised water and dried in an oven for 1 hour at 80 ^{o}C. Varying amounts of clay were used to prepare composites as shown in Table 3.3.

Table 3.3: Amounts of organoclay and sawdust that were used

	Organoclay/ g	Sawdust/ g
1% clay loading	0.03	3.00
5% clay loading	0.15	3.00
10% clay loading	0.30	3.00

3.7 Characterisation

The modified and unmodified clay, sawdust and the nanocomposites were analyzed using FT-IR, XRD and cone calorimetry. The major aim of the exercise was to compare the various samples in order to deduce information regarding the effect of different modifications on the materials as well as nanocomposite preparations.

3.7.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared analysis was carried out on a Perkin Elmer System 2000 FTIR in order to check for any conversion of functional groups in the starting materials and to determine whether the clay and sawdust were incorporated into the materials prepared resulting in a change of functionality altogether. A resolution of 4 cm^{-1} and 32 scans in the range of 370-4000 cm^{-1} were used with the KBr disc technique.

3.7.2 X-Ray Diffractometry (XRD)

The interlayer d-spacing of the clays was investigated by X-Ray diffraction using a Bruker AXS D8 Advance diffractometer (Cu K radiation with λ = 1.5406 Å), equipped with a PSD Lynx-Eye Si-strip detector with 196 channels. This was carried out in locked couple mode at room temperature with an accelerating voltage of 40 kV and current of 40 mA.

XRD was used to determine any shifts in the 2 theta angles as well as the wide angle spectra,. and the type of nanocomposites that were formed. In particular, this was also to determine whether the solution blending process resulted in exfoliated nanocomposites.

3.7.3 Cone Calorimetry

The samples were also analyzed on a CAL2K ECO Isothermal bomb calorimeter.in order to determine the calorific values of the materials. The calorimeter used is shown in Figure 3.1.

Figure 3.1: The CAL2K ECO Isothermal bomb calorimeter used in the study

The oxygen pressure was 3000 kPa, and the operating temperature was 0-60 ^{o}C, with a temperature resolution of 0.000001 ^{o}C. The repeatability was 0-1% RSD and the operation power was 90-260 VAC. Cone calorimetery is used to study the fire behaviour of small samples of various materials in condensed phase. The device allows a fuel sample to be exposed to different heat fluxes over its surface. The measurements of calorific values are based on Huggett’s principle, which states that the gross heat of combustion of any organic material is directly related to the amount of oxygen required for its combustion. The calorific value of a substance is the amount of heat released during the combustion of a specified amount of the substance. Each substance has a characteristic calorific value. It is measured in units of energy per unit of the substance, usually mass. The most common unit used is MJ/kg. It was investigated to check whether modification had any effect on the energy values of the starting material in any way. The flammability of the samples, including the time that a representative sample would take to ignite and burn out was also investigated.

3.7.4 Thermogravimetric Analysis

Themogravimetric analysis (TGA) was used to measure the amount and rate of change in the mass of the samples as a function of temperature and time, in a nitrogen and oxygen atmosphere. A Perkin Elmer thermogravimetric analyzer (TGA7) fitted with a thermal analysis controller (TAC7/DX) was used and the heating rate was 20 °C per minute from 20 °C to 900 °C.

The main applications of thermogravimetric analysis include: compositional analysis of multi-component materials or blends, thermal stability, oxidative stability, estimation of product life times, decomposition kinetics, effects of a particular reactive atmosphere on materials as well as the moisture and volatiles content of materials. The TGA curve is sigmoid, indicating that most of the mass loss occurs at a particular temperature over a narrow range of temperature where the curve slope is greatest. However, the thermal event commences before the region of greatest mass loss and continues after it (Kasidis 2010). This kind of data is therefore more conveniently computed as a derivative of the original TGA curve (rate of mass loss plotted against temperature or time) in order to give a DTG curve, thus the spread of a thermal reaction over a broad temperature appears as a peak. The DTG curve helps in situations where two or more thermal events overlap within similar temperature changes. Slow processes with other fast processes super-imposed, appear as gradient changes in the DTG curve. The DTG curve can, therefore, theoretically characterize overlapping thermal events. The curve's peak area is proportional to the corresponding mass loss, therefore the relative mass losses can be compared.

In this study, the measurements were used to determine the thermal and oxidative stabilities of the materials as well as their composition.. The TGA analyzed the materials' mass loss due to decomposition, oxidation and loss of volatiles.

3.8 References

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CHAPTER 4

4. Characterisation of raw and prepared materials

Characterisation of the various materials was carried out using FTIR and XRD analysis.

4.1 FT-IR analysis

Figure 4.1 shows the FTIR spectra of the various forms of clay: the unmodified clay, the sodium salt and the surfactant modified montmorillonite.

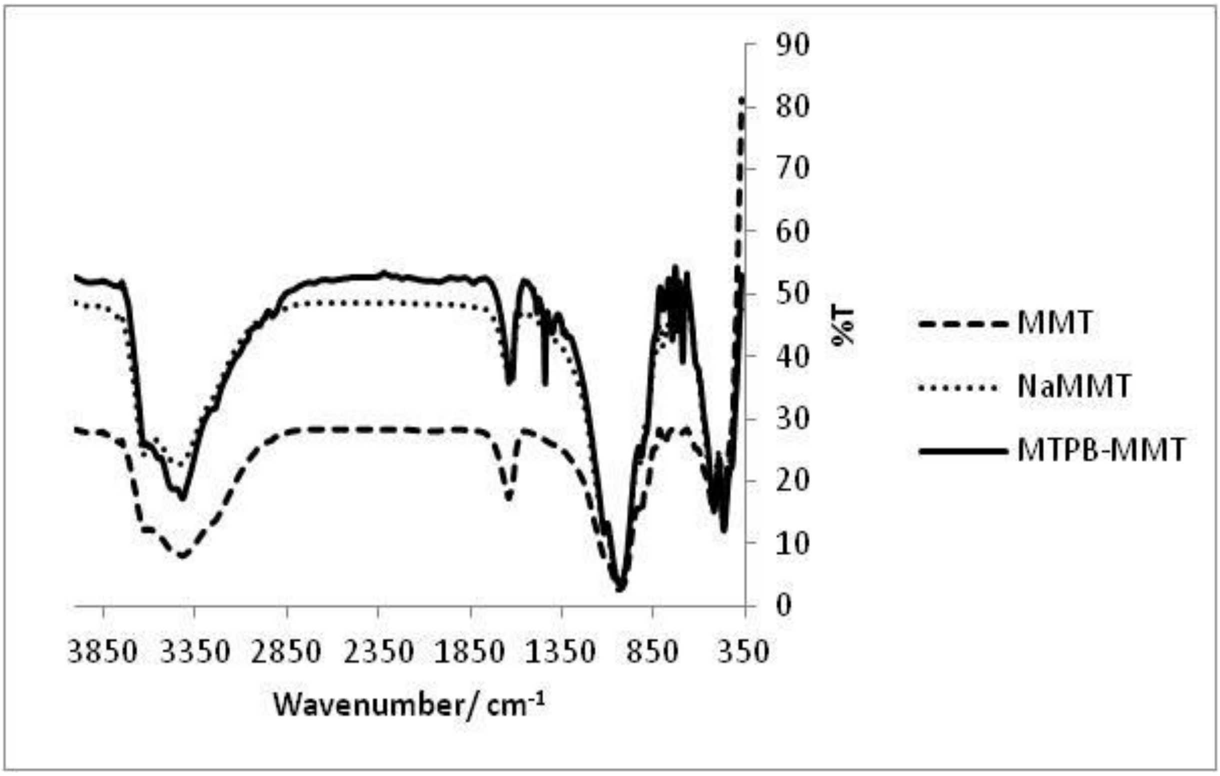

Figure 4.1: The FT-IR peaks of montmorillonite, mono-ionic montmorillonite and organically modified montmorillonite

The infrared spectra of the various samples show several functional groups, as expected. For montmorillonite clay, the broad band at 3414 cm^{-1} was due to –OH stretching mode of interlayer water. The band around 3600 cm^{-1} was due to the –OH stretching mode of Al-OH and Si-OH. The shoulders and the broadness of the –OH bands were mainly due to the contributions of several structural –OH groups that occurred within the structure of montmorillonite. The peak at 1639 cm^{-1} was due to –OH bending mode of adsorbed water. The characteristic peak around 1039 cm^{-1} was attributed to the Si-O stretching (in plane) vibration of layered silicates. The peak at around 900 cm^{-1} was attributed to the Al-Al-OH bending vibration.

Besides showing the relevant peaks for montmorillonite in the IR spectrum of organically modified clay, the small peak at 2926 cm^{-1} was ascribed to the asymmetric and symmetric vibration of the methylene $(CH_2)_n$ groups of the quaternary phosphonium cation, whose structure is shown in Figure 4.2. The peak around 3100-3000 cm^{-1}, due to $C\text{-}C_{stretch}$ vibrations from the aromatic rings was evident, although it was somewhat overshadowed by the C-H absorption peaks. However, other typical aromatic peaks around 1400-1600 cm^{-1} and around 700 cm^{-1} were present, thus signifying a successful modification by the surfactant.

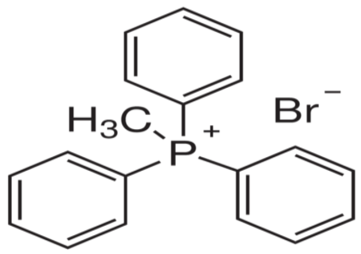

Figure 4.2: The structure of methyl triphenyl phosphonium bromide

The characteristic peak at around 1032 cm^{-1} was attributed to an in-plane Si-O stretching for layered silicates. (Calisterios 2009)

The introduction of the organic surfactant in the interlayer d-spacing caused a $-CH_2$ asymmetric stretching band shift to 2926 cm^{-1} and $-CH_2$ symmetric stretching band at 2854 cm^{-1}. This observation was reported in studies by Zhu and co-workers (Zhu, et al. 2005) and was said to be due to a liquid-like molecular environment of the intercalated surfactant. The infrared spectra in the regions of 1467 cm^{-1} and 779 cm^{-1} presented only one peak that is related to either molecular environment or disordered arrangement, where the alkyl chains rotate freely around the long axis (Casal, et al. 2002). The IR spectrum of purified sawdust is shown in Figure 4.3.

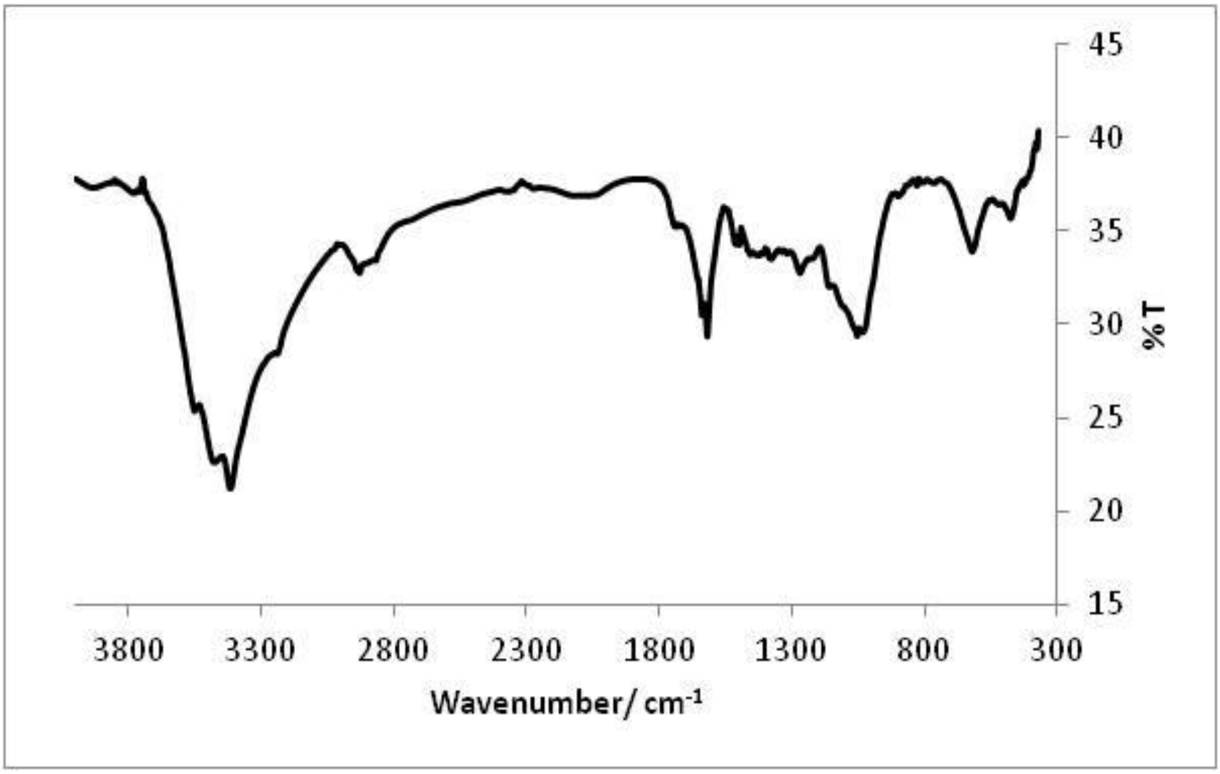

Figure 4.3: IR spectrum of sawdust

An -OH stretching mode at 3451 cm^{-1} was due to the -OH stretching of the sugars present in the wood. There was also a C-H stretching absorption at 2928 cm^{-1}, due to the presence of alkyl chains in the wood. The peak at 1618 cm^{-1} is due to an –OH bending mode of adsorbed water. The C-O stretching mode showed a characteristic absorption at 1053 cm^{-}.[1]

The IR spectrum of the nanocomposites showed that the functional groups observed in both the wood and clay were present. The FTIR spectra of the nanocomposites with different clay loadings of unmodified clay are shown in Figure 4.4.

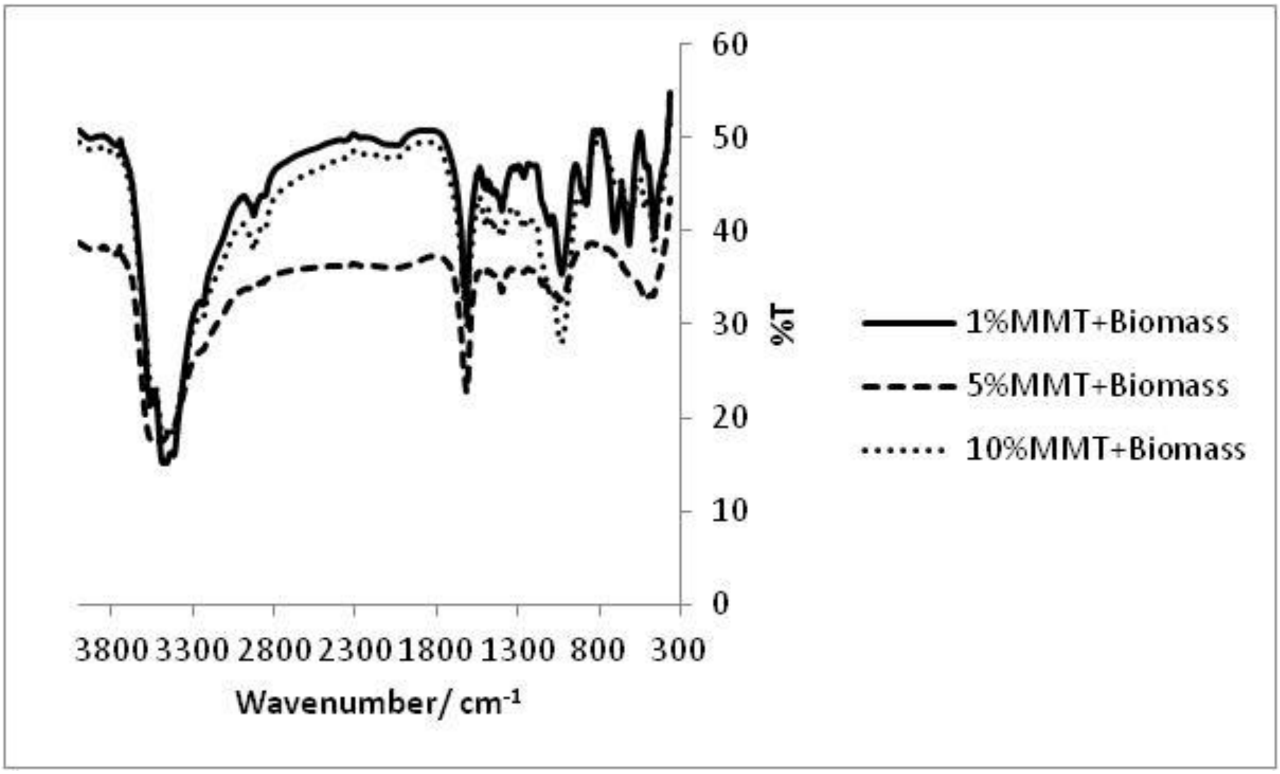

Figure 4.4: The FT-IR plots for nanocomposites of sawdust and different loadings of unmodified montmorillonite

Figures 4.5 and 4.6 show the FTIR spectra of nanocomposites derived from biomass with the monoionic salt of clay and with the surfactant, respectively.

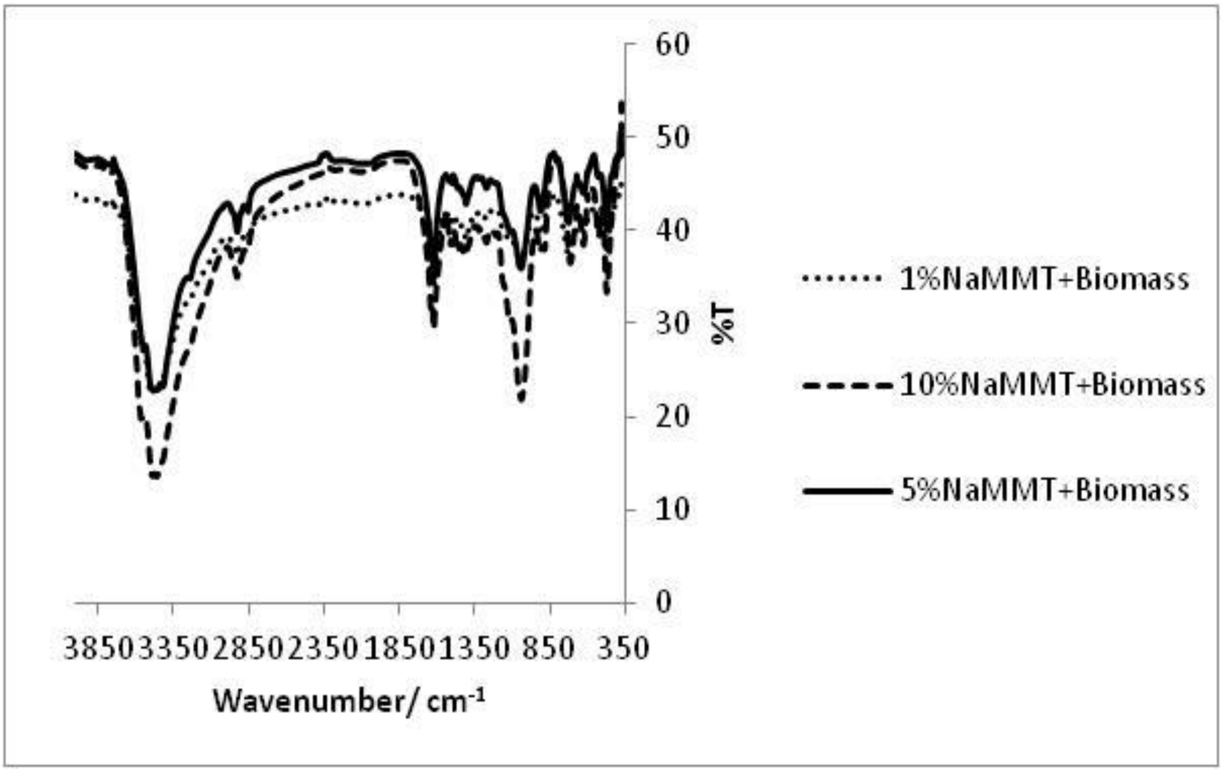

Figure 4.5: FT-IR plots of nanocomposites mono-ionic montmorillonite and biomass

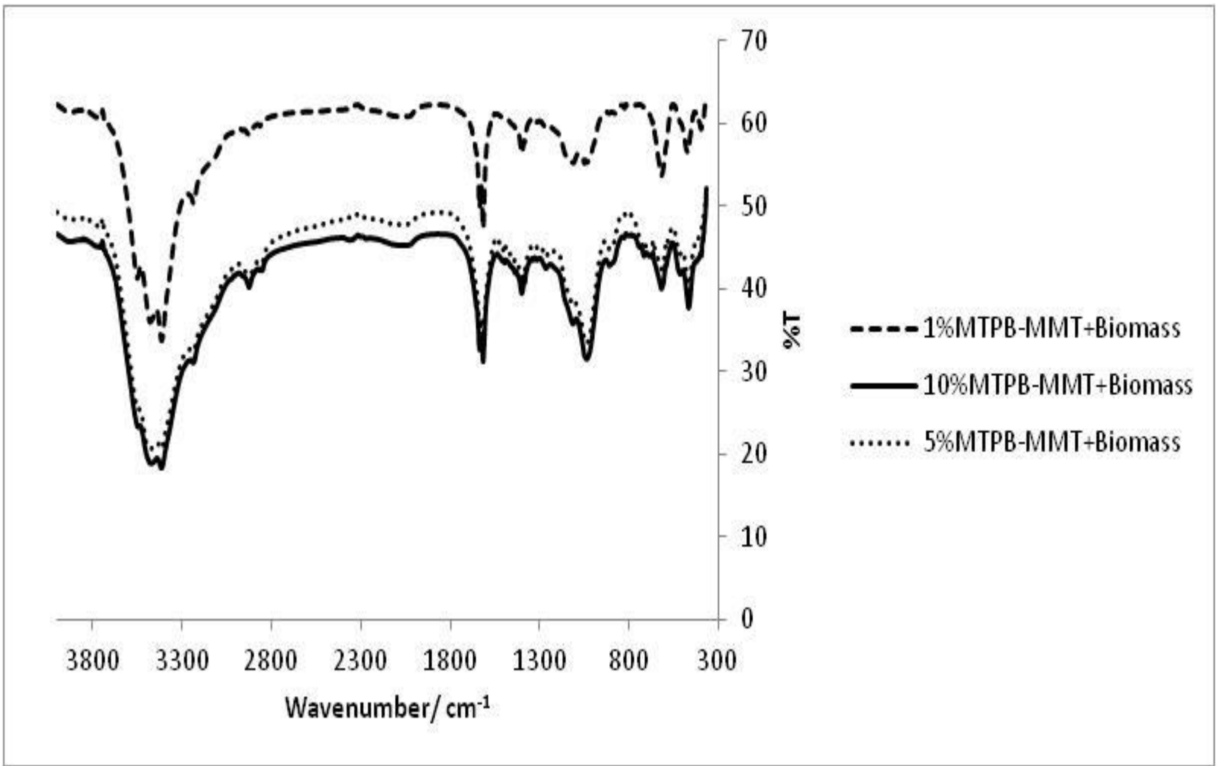

Figure 4.6: FT-IR plots of montmorillonite clay modified with methyl triphenyl phosphonium bromide and sawdust

4.2 XRD analysis

The XRD spectra of unmodified and surfactant-modified clays are shown in Figure 4.7.

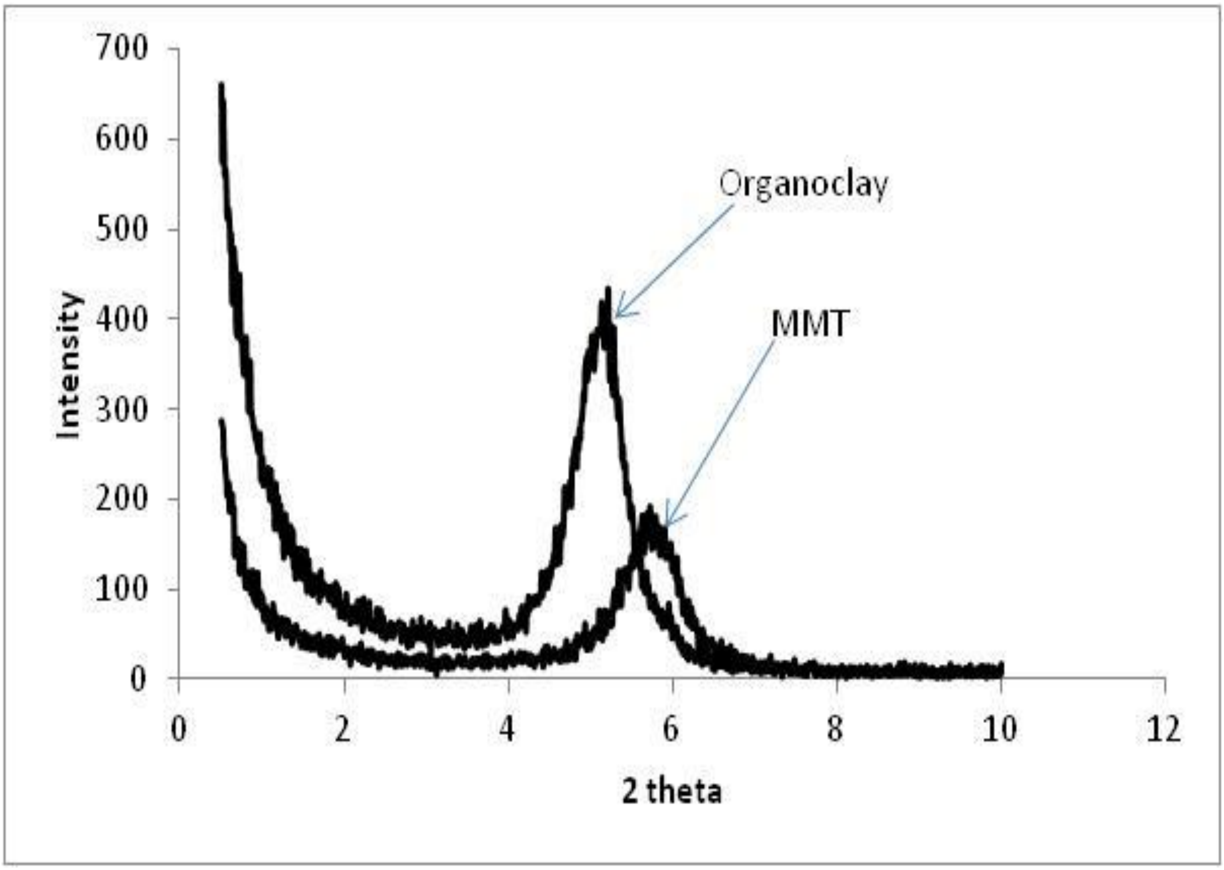

Figure 4.7: XRD plots of unmodified clay and organically modified clay

XRD analysis was carried out using a Bruker AXS D8 Advanced Diffractometer. X-ray diffraction was used to study the changes in the basal spacing of montmorillonite when it was modified with organic surfactant and when it was combined with wood to make a nanocomposite.

If total destruction of the layered structure of clay occurs, no peak would be observed in the lower 2 theta region. The angle shifts to lower values if the interlayer d-spacing increases, according to Bragg's law. The interlayer d-spacing changed with the basal spacing of the montmorillonite when it was modified with methyl triphenyl phosphonium bromide. This spacing is measured from the top of a Si-tetrahedral silica sheet to the top of the Si-tetrahedral sheet of the next layer. The different basal spacings of the montmorillonite and its hybrids are a function of the interlayer cation as well as the surface charge and the hydration state of the montmorillonite (MacEwan and Wilson 1980). The linkage between organic cations and the silica surface of the clays is fundamentally electrostatic in nature but physical non-coulombic forces can also contribute to their adhesion to the clay (Newman 1987).

The modification of clay to organoclay increased the interlayer d-spacing of the clay. This is consistent with the fact that the organic surfactant is bulky as observed in Figure 4.2 when compared to the inorganic cations that it replaced. The 2 theta value was lowered as the intensity increased, as expected. This was attributed to the fact that exfoliation took place to a significant extent. The wood sufficiently displaced the clay layers, leading to separate sheets instead of layers. The 2θ values and their intensities are summarised in Table 4.1 and the XRD spectra of the nanocomposites from unmodified clay are shown in Figure 4.8.

Table 4.1: Summarised XRD data for the montmorillonite and organoclay

Clay type	**2θ**	**Intensity**
MMT	5.72	192
MTPB-MMT	5.21	433

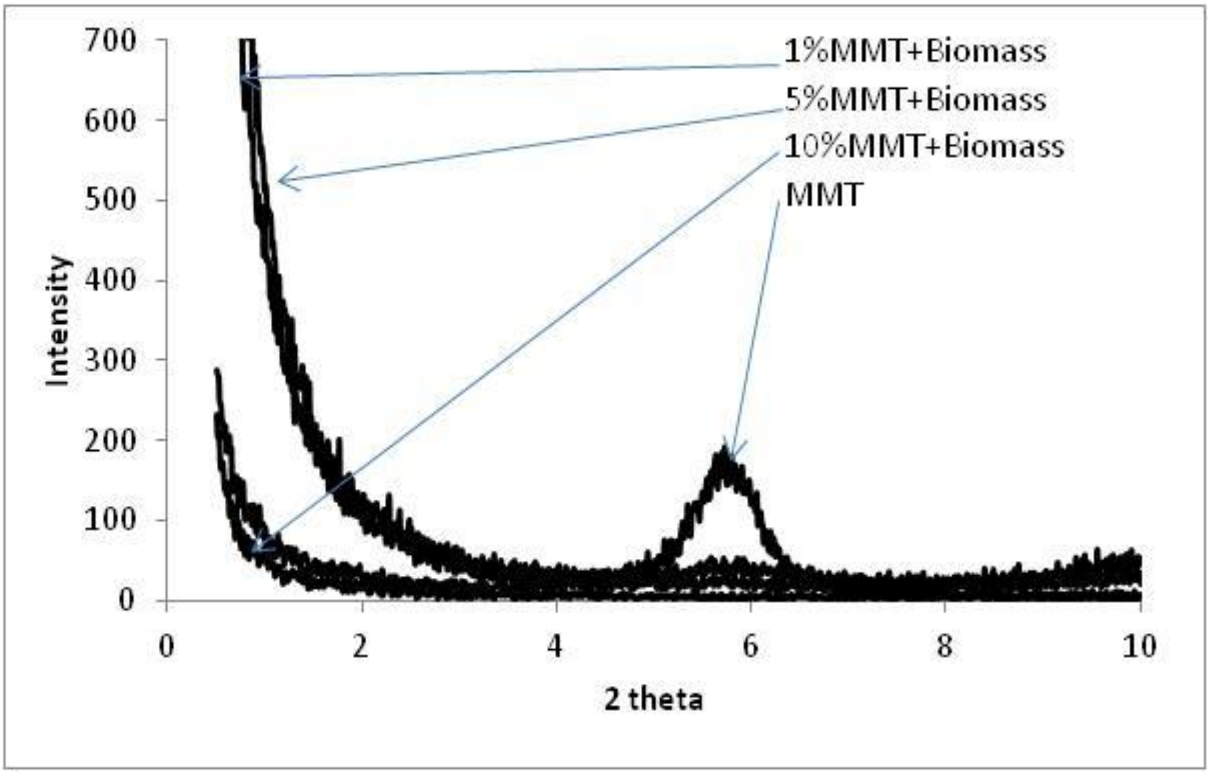

Figure 4.8: XRD plots of nanocomposites of biomass and unmodified montmorillonite

When unmodified montmorillonite was compounded with sawdust, there was almost complete exfoliation, as interpreted from the absence of a peak in the lower 2 theta angle in Figure 4.8. This phenomenon was also observed when the biomass was compounded with mono-ionic montmorillonite, as shown in Figure 4.9 below. Figure 4.10 shows the XRD plots of the nanocomposites prepared using the organically modified clay.

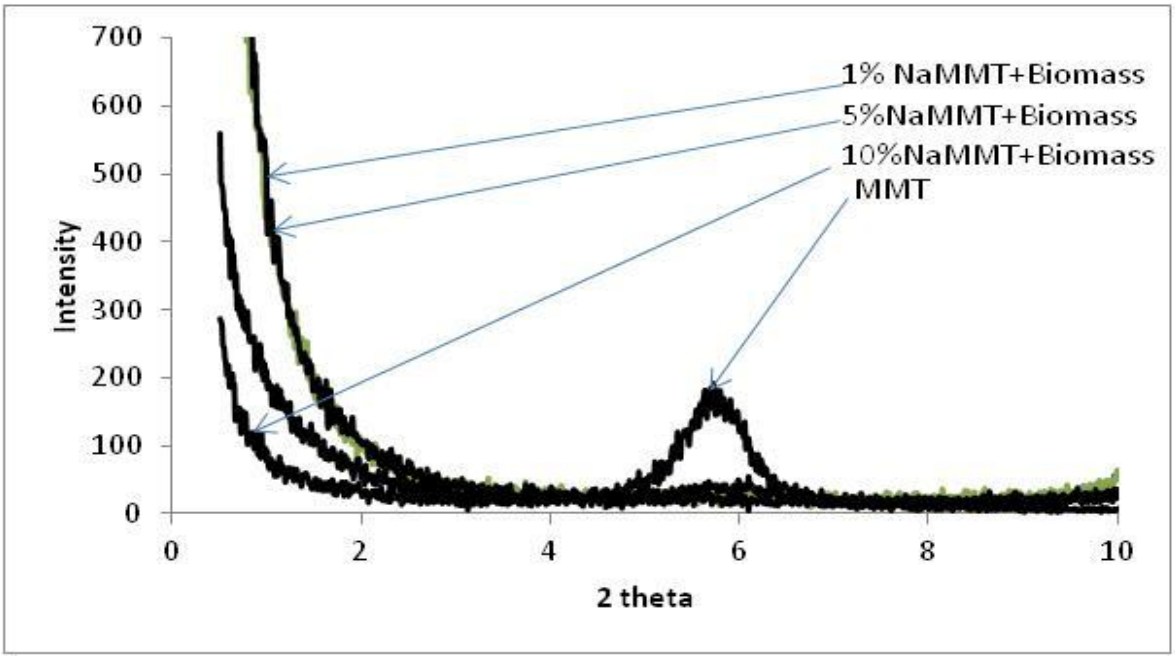

Figure 4.9: XRD plots of nanocomposites of mono-ionic montmorillonite clay and sawdust

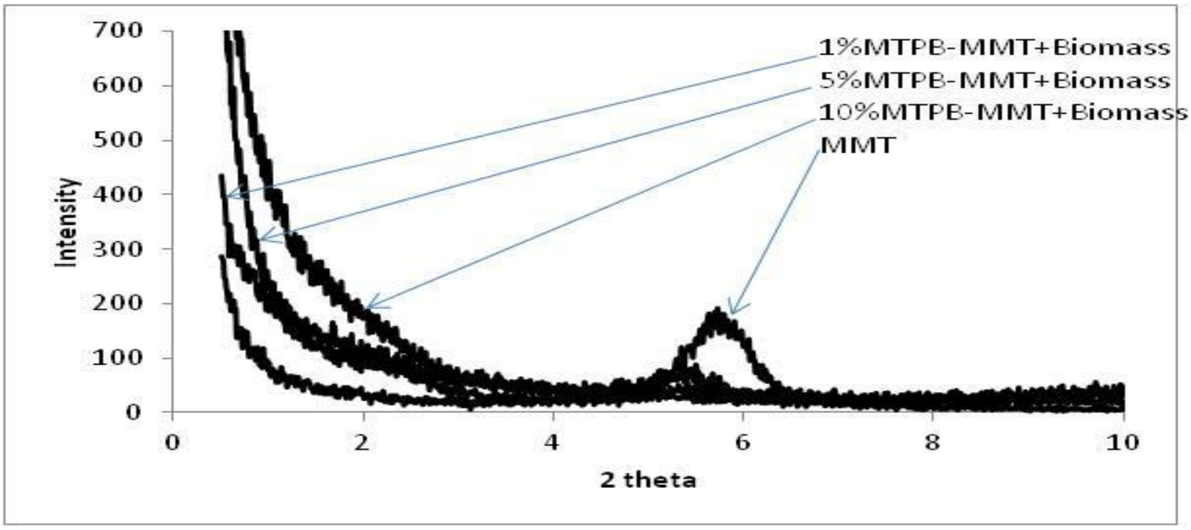

Figure 4.10: XRD plots of organically modified clay combined with sawdust

The XRD pattern of the nanocomposites, which had organically modified clay also showed exfoliation. The wide angle diffraction patterns of the clay and the nanocomposite are shown in Figure 4.11 and Figure 4.12, respectively.

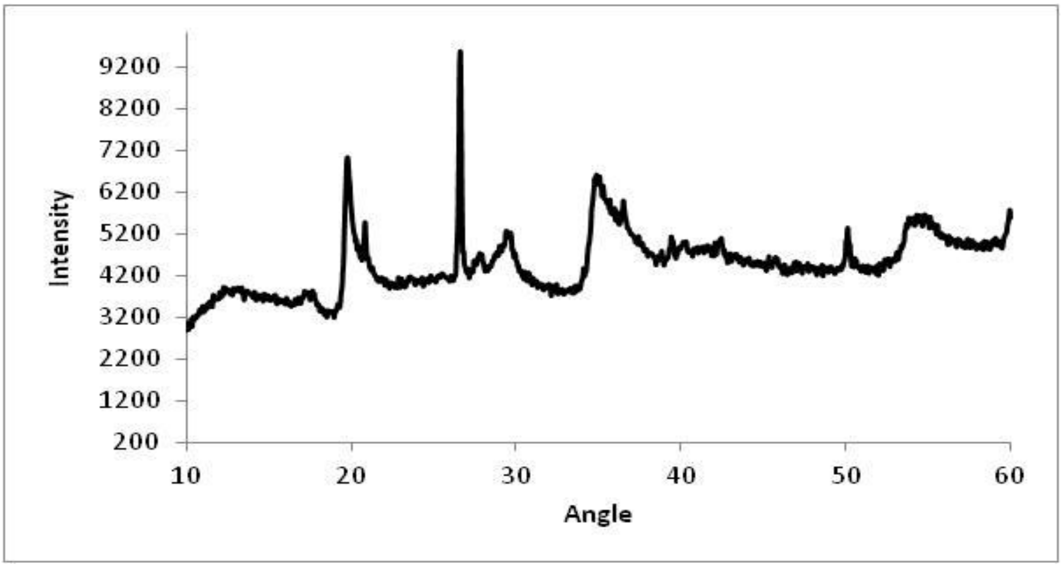

Figure 4.11: Wide angle diffraction pattern of unmodified montmorillonite

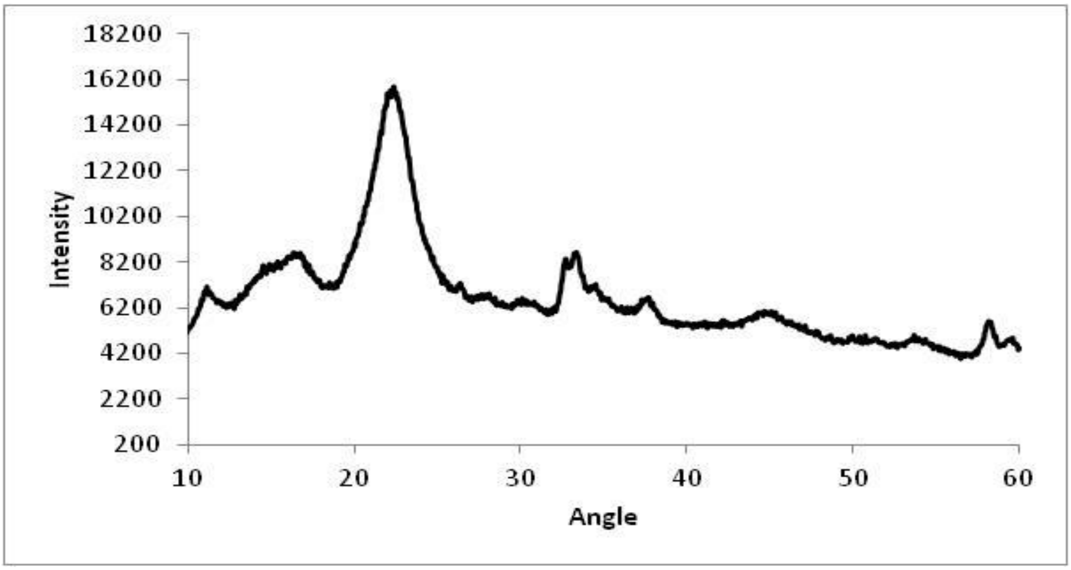

Figure 4.12: Wide angle diffraction pattern of biomass and clay nanocomposite

Some of the peaks observed for montmorillonite were not observed in the XRD pattern of the nanocomposite, meaning that there was a significant structural change which took place. The lower 2 theta values in the nanocomposite were not as pronounced as those found on the clay, which shows some degree of interaction between the clay and sawdust matrices.

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CHAPTER 5

5. Thermal properties of unmodified, modified and nanocomposite materials

5.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out in a stream of nitrogen gas and air, using a Perkin-Elmer TGA 7 instrument. The heating rate was 20 ^{o}C per minute and heated to 900 ^{o}C from room temperature, while the flow rate of the gas was 20 mL per minute.

This analytical method utilises a sensitive balance to determine the weight loss of a sample through a temperature range. The sample is loaded onto a pan and then placed on the balance. A furnace then encloses the sample and the temperature is increased at a pre-programmed rate in a controlled environment of selected gases. Constituents of the sample decompose at different rates.

5.1.1 Weight loss with temperature increase

Figure 5.1 shows the weight versus temperature thermogram for unmodified sawdust. This sawdust was from pine wood, composed of 79% combustibles and 21% water and ash.

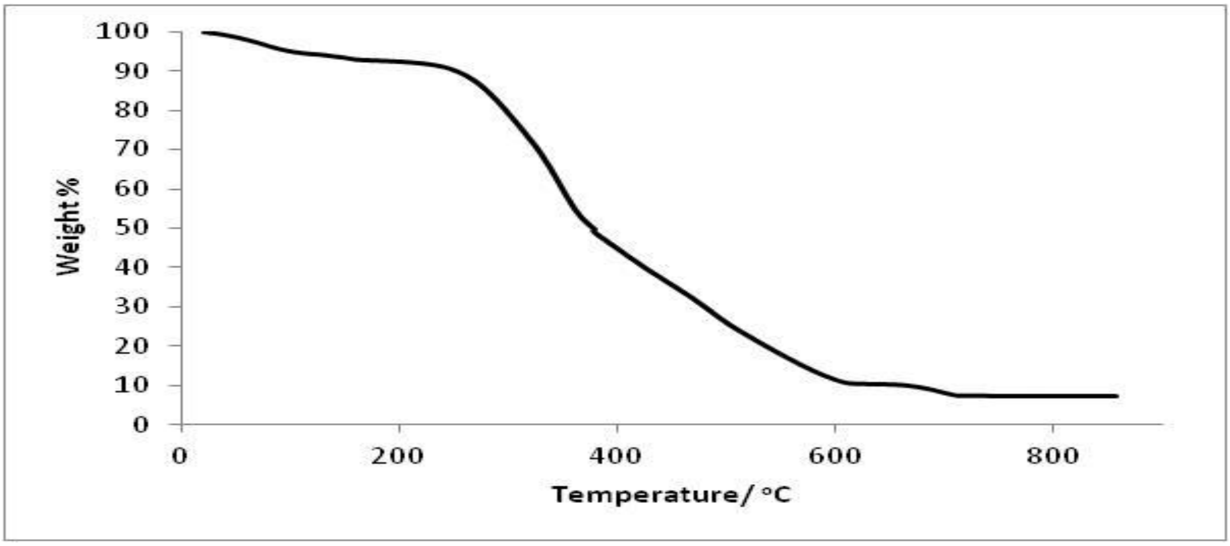

Figure 5.1: TGA of sawdust

The first weight loss observed, just after 100 °C, is due to water present in the wood boiling off. At 232 °C, the wood particles begin evolving volatiles. The volatiles include hydrogen, methane, ethylene, ethane, benzene and carbon monoxide (Ecofire 2012). Carbon ignites between 400 °C and 600 °C and the volatiles ignite between 537 °C to 704 °C. Figure 5.2 shows a thermogram of the various types of clay that were used.

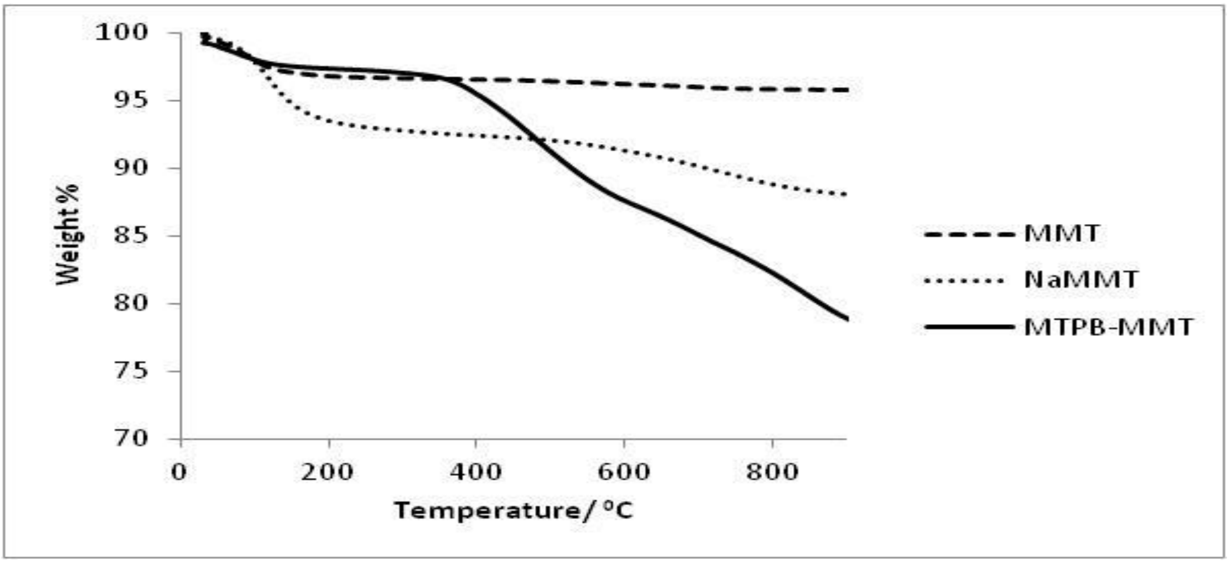

Figure 5.2: TGA plot of the various modes of clay that were used

The TGA curves for raw montmorillonite, modified montmorillonite and the nanocomposites start from 0 ^{o}C to 900 ^{o}C. The decomposition occurred in four distinct steps. The removal of adsorbed water and volatile organics occurred below 100 ^{o}C. From 100 ^{o}C weight loss was mainly due to decomposition of the carbonates in the organoclay and loss of interlayer water. Between 500-700 ^{o}C, dehydroxylation occurred, while residual carbonaceous product formation occurred above 700 ^{o}C, as reported by Xi and co-workers (Xi, et al. 2004).

The thermogram for organically modified clay showed that the amount of free and interlayer water in montmorillonite had decreased, as shown in the section between 100-500 ^{o}C. The decrease in the amount of free and interlayer water resulted from the replacement of hydrated cations by the surfactant. Two distinct types of water are present in montmorillonite. The first type is the adsorbed water owing to the larger specific surface area of clay. This water possesses great mobility and it can be lost easily. The second type constitutes the hydration shell around the exchangeable cations. Its presence depends on the number of hydrated cations residing in the interlayer space. (X. F. Xi, et al. 2005) Figure 5.3 shows the thermograms of nanocomposites of unmodified clay and sawdust.

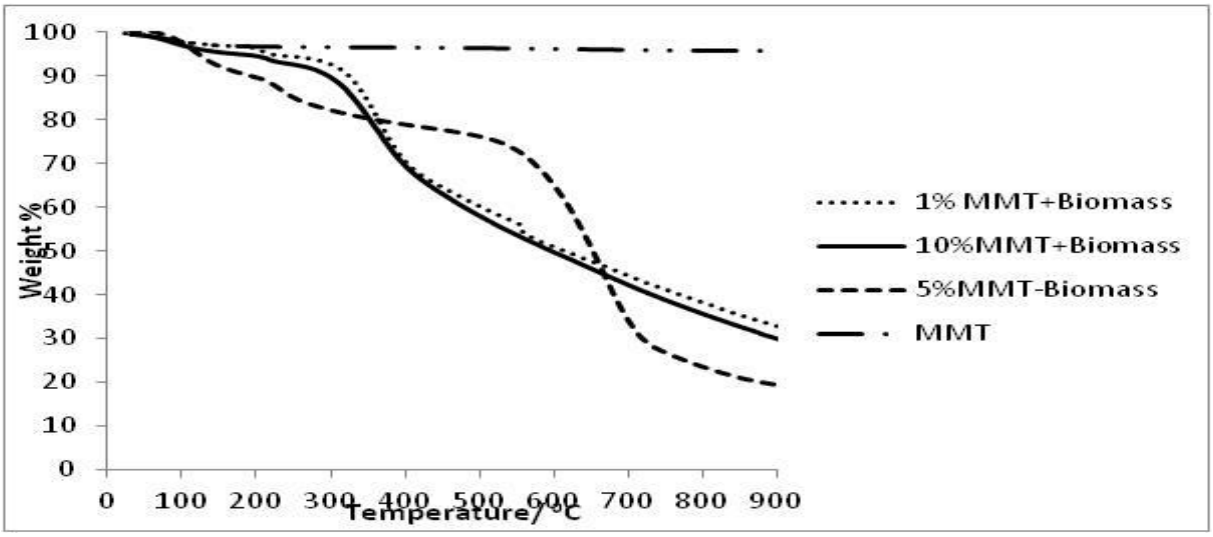

Figure 5.3: TGA plot of nanocomposites of unmodified clay and biomass

From Figure 5.4, it is apparent that adding 5% of sodium-montmorillonite to the sawdust resulted in a better thermal stability. After the analysis, 35% percent of residue was present, which is a significant improvement on the residues when compared to unmodified sawdust which has less than 10% of residue. After one hour of analysis, 5% and 10% loadings of sodium-montmorillonite had the highest amounts of residue, at 38.3% and 44.3%, respectively. All the three different clay loadings still showed a significant rise in the ash content; even for the loading of 1% organoclay, which had the least amount of residue at 16.7% of the starting material at the end of the TGA analysis.

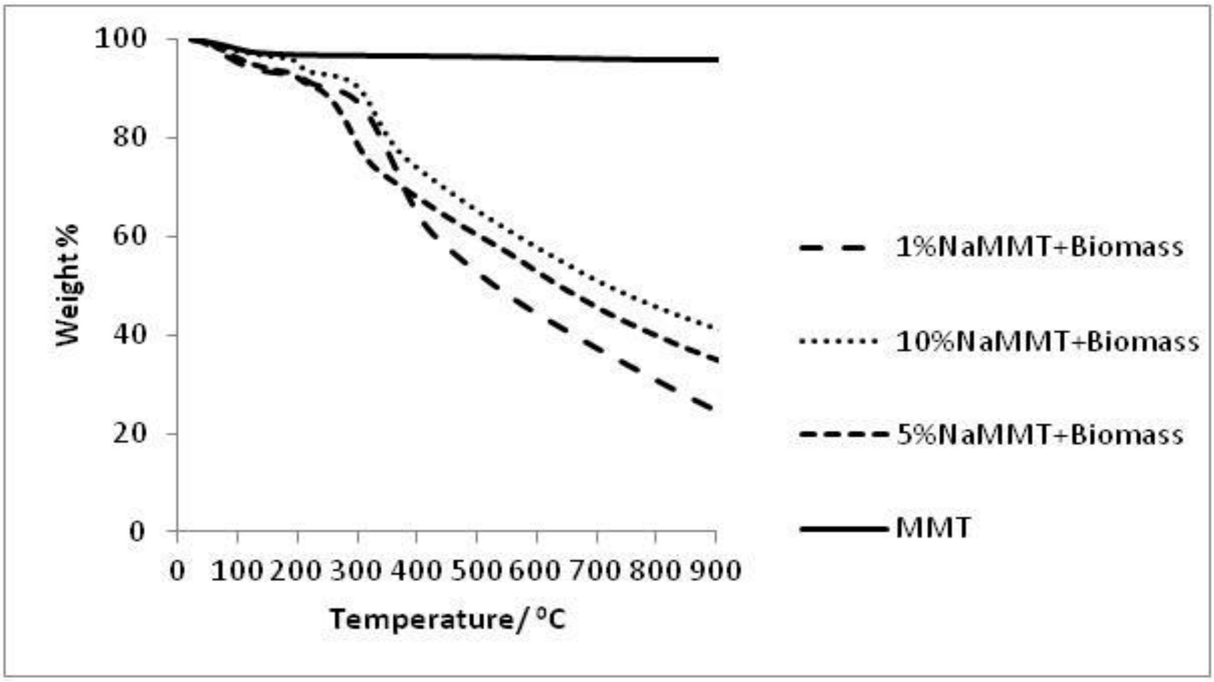

Figure 5.4: TGA plot of biomass composited with mono-ionic montmorillonite

Pine wood is composed of 79% combustibles and 21% water and ash. Firstly, the water boils off and then at 232 °C, the wood particles begin evolving volatiles. Carbon ignites between 400 °C and 600°C and the volatiles ignite between 537 °C to 704 °C. The volatiles include hydrogen, methane, ethylene, ethane, benzene and carbon monoxide (Ecofire 2012). All the three loadings showed a twofold increase in the amount of residue when compared to unmodified sawdust.

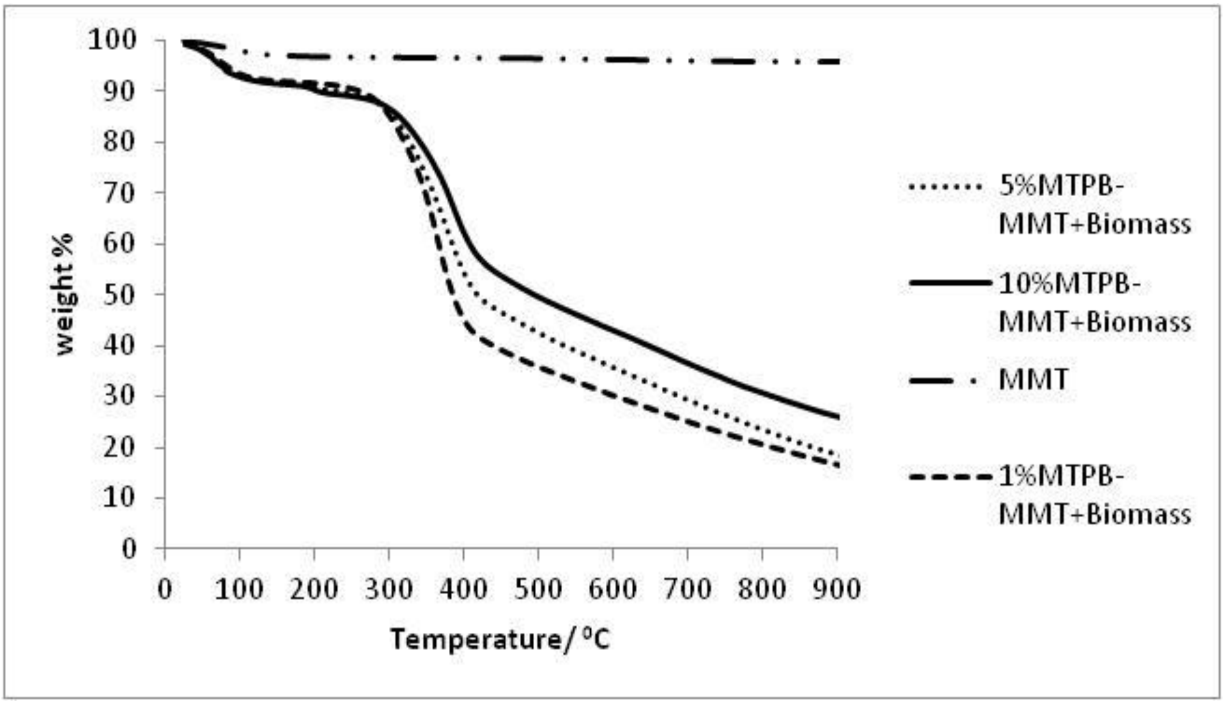

Figure 5.5: TGA plot of organically modified clay composited with sawdust

The apparent increase in the residue after the thermal events was also noticed in the sawdust that was modified with organically modified clay. There was a sharp weight loss just below 420 ^{o}C, which was attributed to the presence of the long chain of combustible hydrocarbons present in methyl triphenyl phosphonium bromide. The amounts of residue in each nanocomposite are summarised in the Table 5.1 below.

Table 5.1: Amounts of residue realised on TGA

Material	% residue at 40 minutes	% residue at 400 ^{o}C	% residue at 900 ^{o}C
Sawdust	4	33.0	5.1
Montmorillonite	95.7	96.5	95.7
Na-Montmorillonite	88.5	92.4	88.1
MTPB-MMT	81.0	95.4	78.9
1% MMT + Biomass	34.0	70.5	32.7
5% MMT + Biomass	22.2	79.0	19.5
10% MMT + Biomass	34.0	69.4	29.9
1%NaMMT+Biomass	28.9	64.8	24.6
5%NaMMT+Biomass	38.3	68.0	35.0
10%NaMMT+Biomass	44.4	73.7	29.4
1%MTPB-MMT+Biomass	19.1	45.0	16.7
5%MTPB-MMT+Biomass	21.9	54.0	18.9
10%MTPB-MMT+Biomass	30.0	62.1	26.0

The biomass which was modified with organoclay produced the least amount of residue when compared to those modified with montmorillonite and mono-ionic montmorillonite. If this can be coupled with longer burning times, this will be desirable; i.e a fuel which burns longer and produces moderate residue.

5.1.2 Weight loss over time

The weight loss over time of the various samples was plotted in Figures 5.6 to Figure 5.9 below.

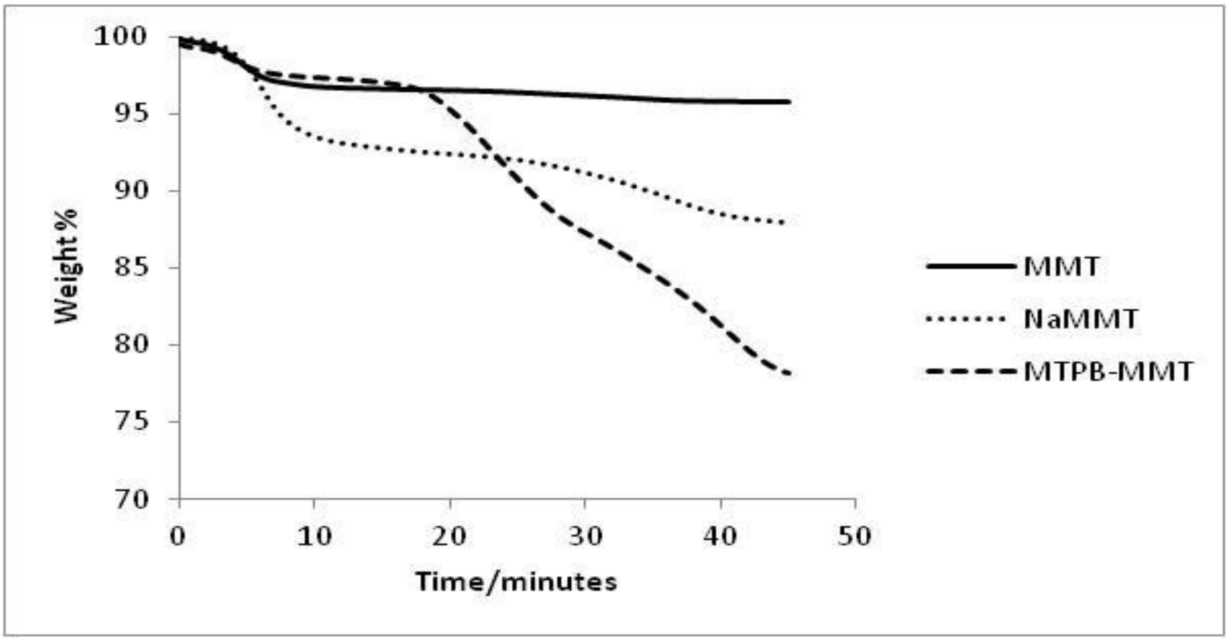

Figure 5.6: TGA plots of the three forms of clay that were used

As shown in Figure 5.6, montmorillonite showed very little weight loss over the entire analysis. This is because it has very little combustible material, most of which is structural water that evaporates at just above 100 ^{o}C, and is present in very little quantities in the clay, nonetheless. As expected, of the three clay forms, organoclay showed the greatest weight loss which is attributed to the presence of the combustible hydrocarbon chain of the methyl triphenyl phosphonium bromide.

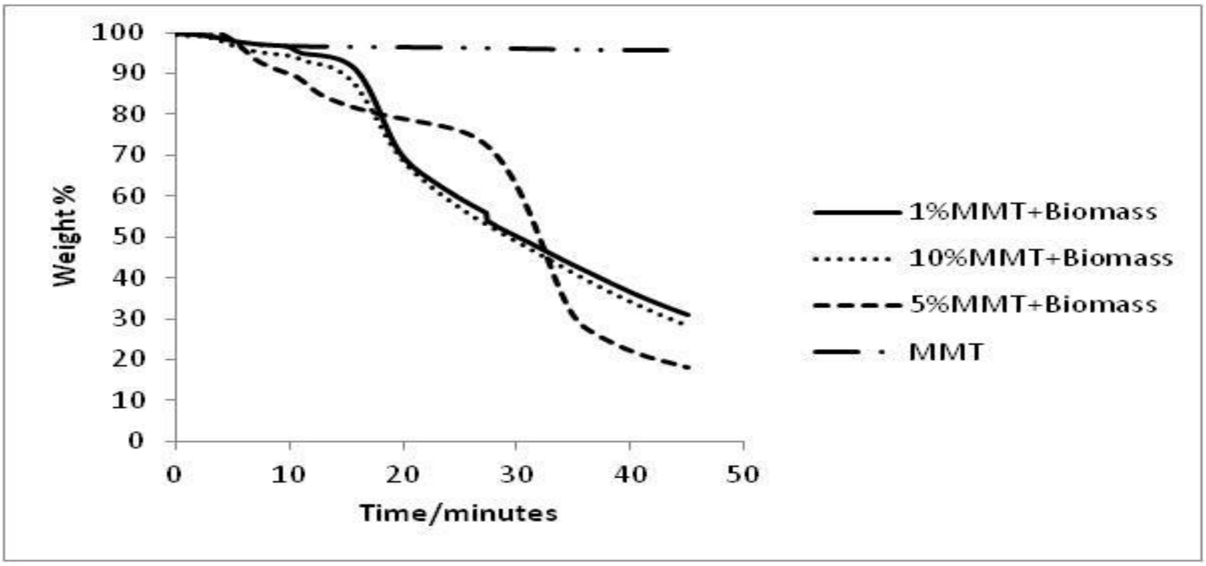

Figure 5.7: ***TGA plots of composited unmodified montmorillonite and biomass***

Figure 5.7 shows the TGA plots of the three levels of loading of montmorillonite; the 1% loading showed the best stability from the beginning of the analysis until the end. Its performance was closely mimicked by that of the 10% loading. The 5% loading started badly in the early stages, showed some promise between 30 and 40 minutes, but finished very disappointingly.

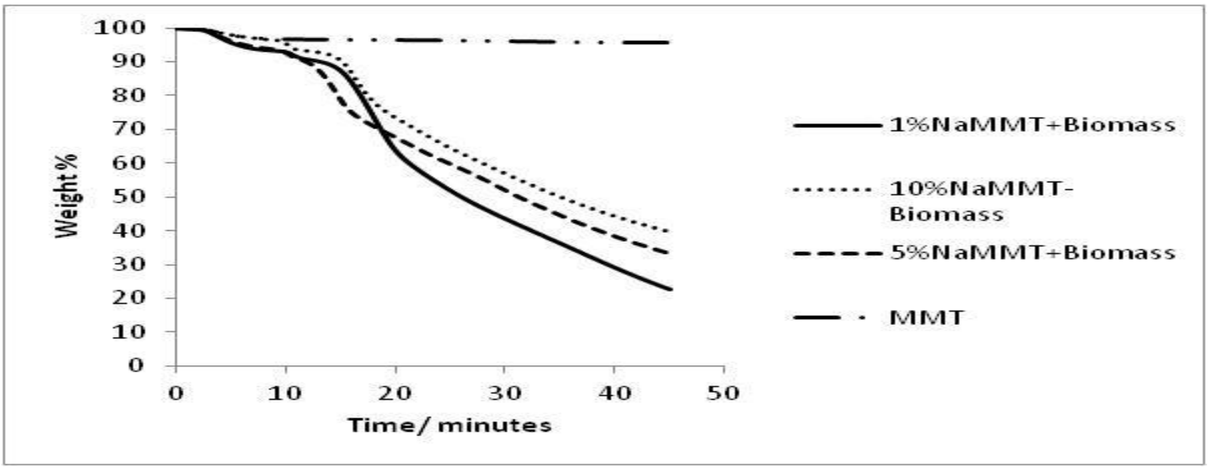

Figure 5.8: TGA plots of mono-ionic montmorillonite composited with biomass

The trend of having the lowest clay loading performing well in terms of thermal stability and more residues did not hold for the sodium montmorillonite and biomass nanocomposites, as shown in Figure 5.8. The highest clay loading of 10% had the best performance with the 1% loading doing badly, and the 5% loading still remaining between these two extremes as was observed for the unmodified clay loadings. However, it is still worth noting that all the three loadings still resulted in better retardation of degradation.

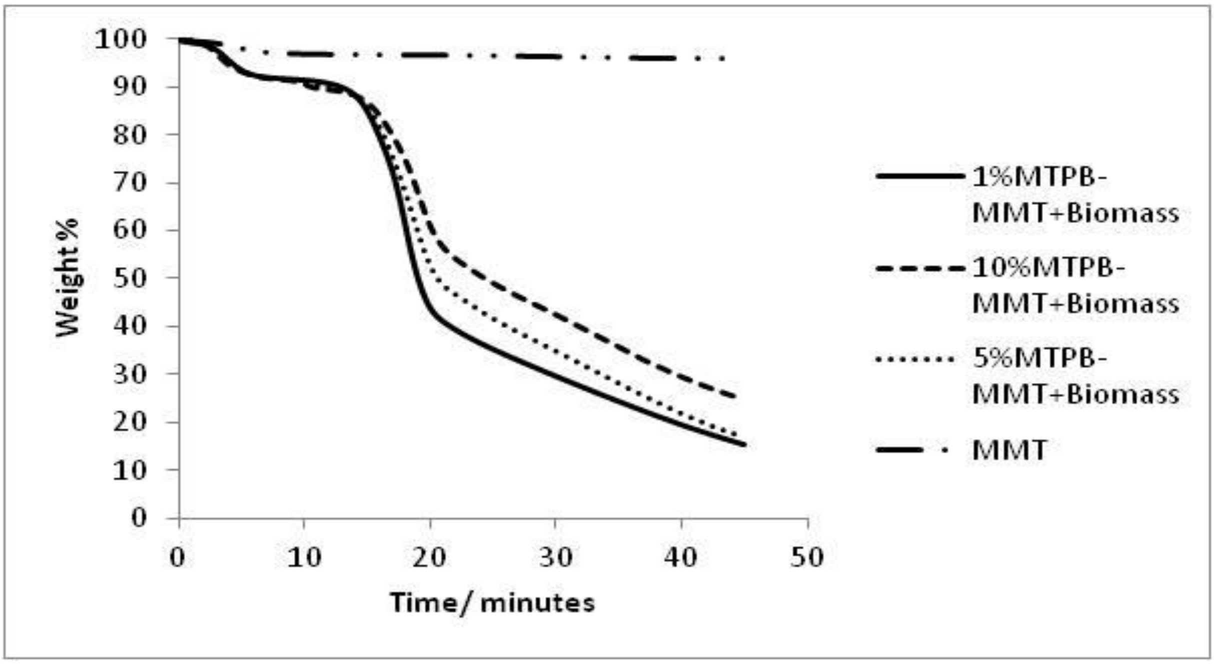

Figure 5.9: TGA plots of biomass composited with organically modified montmorillonite

As shown in Figure 5.9, the organoclay loading of 10% gave the highest amount of residue.

5.1.3 DTG

This subsection deals with the DTG analysis of all the samples.

Figure 5.10 and Figure 5.11 show the DTG plots of montmorillonite and mono-ionic montmorillonite, respectively.

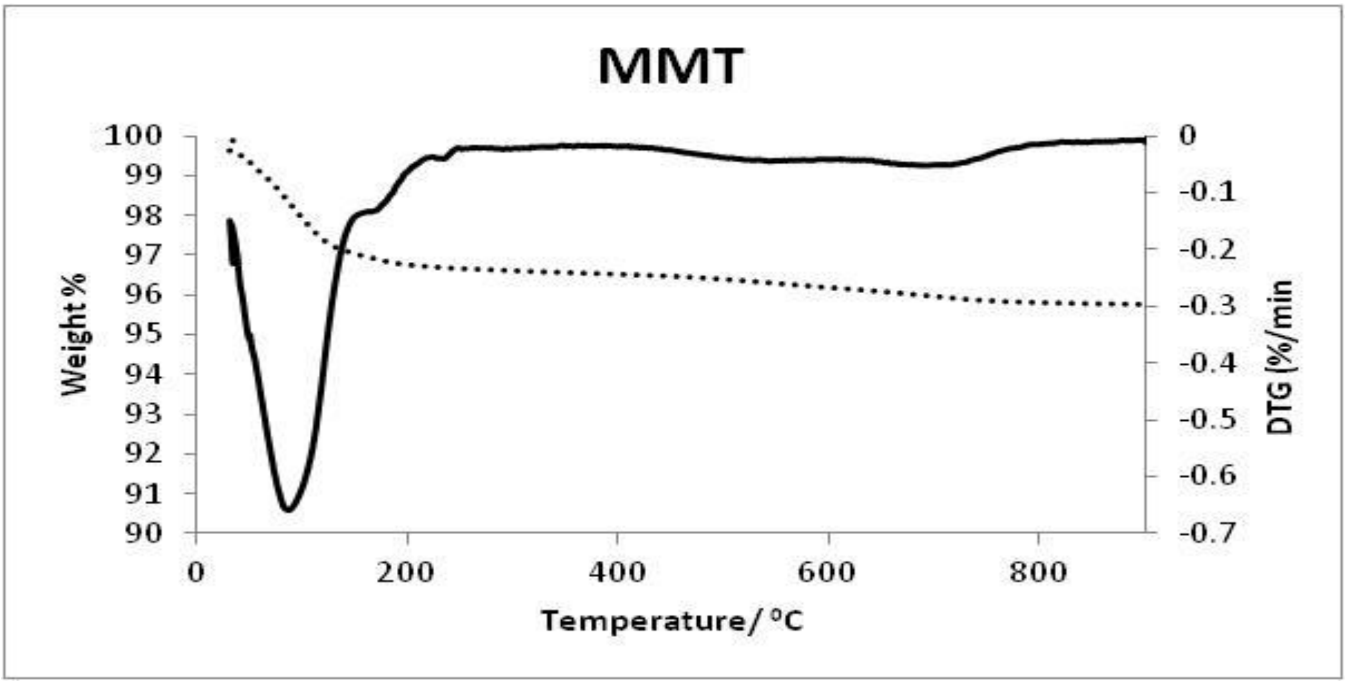

Figure 5.10: DTG plot montmorillonite

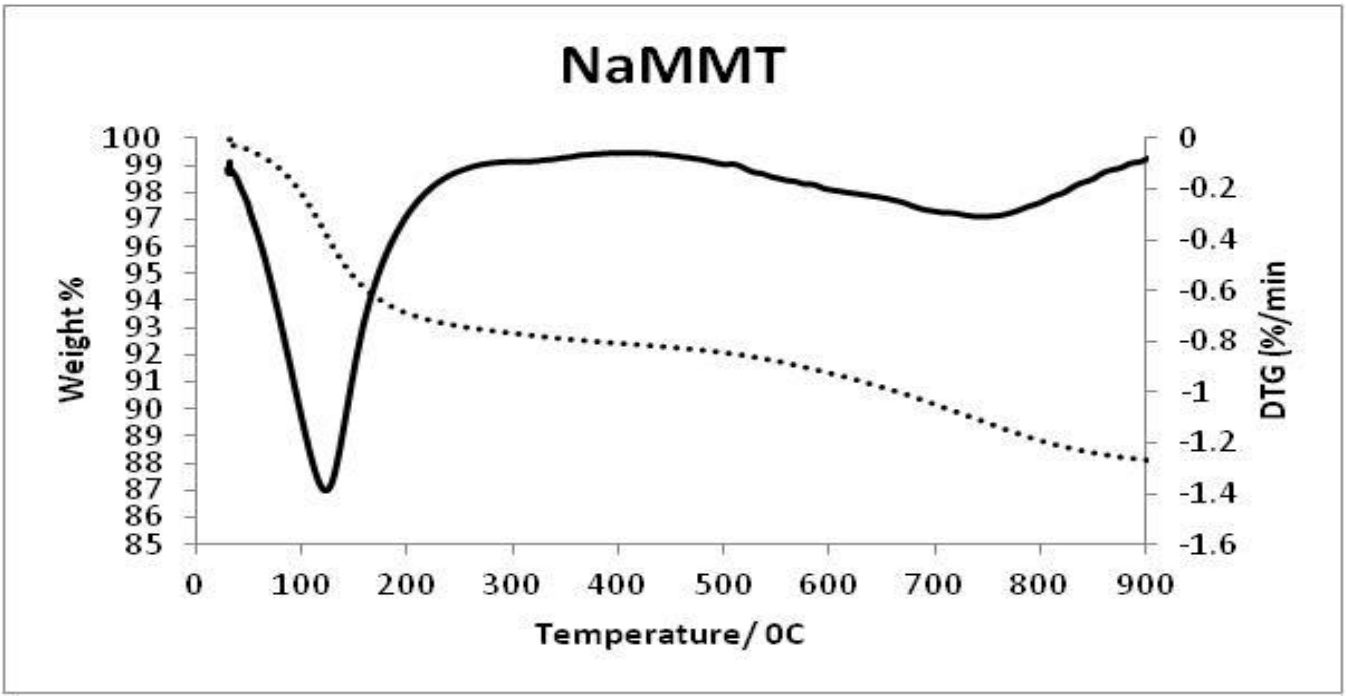

Figure 5.11: DTG plot of mono-ionic montmorillonite

The DTG plot corresponding to sodium montmorillonite shows an endothermic peak at low temperatures, below 150 ^{o}C. It is generally interpreted as being caused by the loss of weakly bonded, physisorbed water adsorbed on the external surface of the clay, and of interlamellar water coordinated to the exchangeable cations, in this case Na. (de Souza Santos 2000). A shoulder visible at 337 ^{o}C arises because of the interlamellar water loss, not easily evolved by diffusion from the sample. The next two peaks appear from dehydroxylation of the clay octahedral layer in different environments; at about 500 ^{o}C from Al substituting Mg (or Fe) and at about 600 ^{o}C from Al (Sun Kou 1998). These endothermic peaks correspond to the losses detected by TGA in the same interval. Finally, an endothermic peak at around 792 ^{o}C is due to the internal dehydroxylation and crystalline net destruction. According to Grim and Rowland (Grim and Rowland 1972), this type of materials should present S-shaped endo-exothermic peaks, the first part corresponding to the loss of structural water without destroying the crystalline net which persists up to higher temperatures and the second part (exothermic peak) to changes constituting a new structure of a-quartz or mullite, depending on the nature of the montmorillonite involved. This second peak is not visible here, probably because the high content of interchanged Na impedes the internal transformation of the clay (Sun Kou 1998).

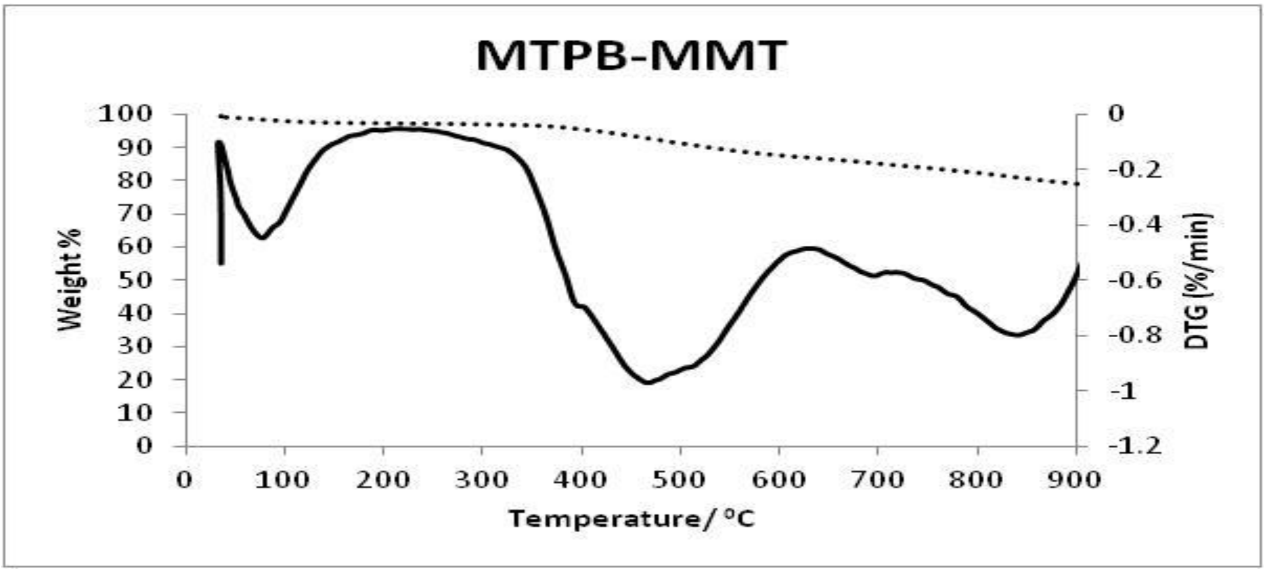

Figure 5.12: DTG plot of organically modified clay

Several studies conducted by Xi and co-workers (Xi, et al. 2005), (Xi, Frost and He 2007), Xu and Boyd, (Xu and Boyd 1995) Tiwari Khilar and Natarajan (Tiwari, Khilar and Natarajan 2008) as well as Marras and co-workers (Marras, et al. 2007), showed that montmorillonite modified by surfactants decomposes in four steps, which are: water desorption, dehydration, surfactant desorption, and dehydroxylation of the organoclay. Sodium-montmorillonite has two distinct peaks. One of them which occurs at about 55 ^{o}C, is attributed to the volatilization of the free water; while the one at 618 ^{o}C is due to the structural water resulting from the dehydroxylation of clay hydroxyl units. In comparison with sodium-montmorillonite, organic montmorillonite has lower mass loss at about 55 ^{o}C, implying less free water in the modified clay. One possible explanation is that the presence of surfactants lowers the surface energy of the inorganic material, and converts the hydrophilic silicate surface to an organophilic type (Marras, et al. 2007). Figure 5.12 shows that the organic montmorillonite has four peaks within the given temperature range. Some of these peaks are not present for montmorillonite and sodium-montmorillonite, implying that they did not undergo thermally-induced changes in that temperature range. The extra peaks in the organic clay in this temperature range should therefore be attributed to mass loss due to the decomposition of the surfactant. (X. F. Xi, et al. 2005) It can be found that there are four molecular environments of the surfactant in the organic montmorillonite. The first peaks occurred between 160 to 175 ^{o}C and are attributed to the decomposition of the surfactant that is physically absorbed on the external surface of the montmorillonite. The second peaks take place between 400–550 ^{o}C and are due to the decomposition of interlayer-adsorbed surfactant molecules. The last two peaks at about 700 ^{o}C and between 850–860 ^{o}C, correspond to the decomposition of two kinds of intercalated surfactant cations with different molecular environments. (Zhou, et al. 2009)

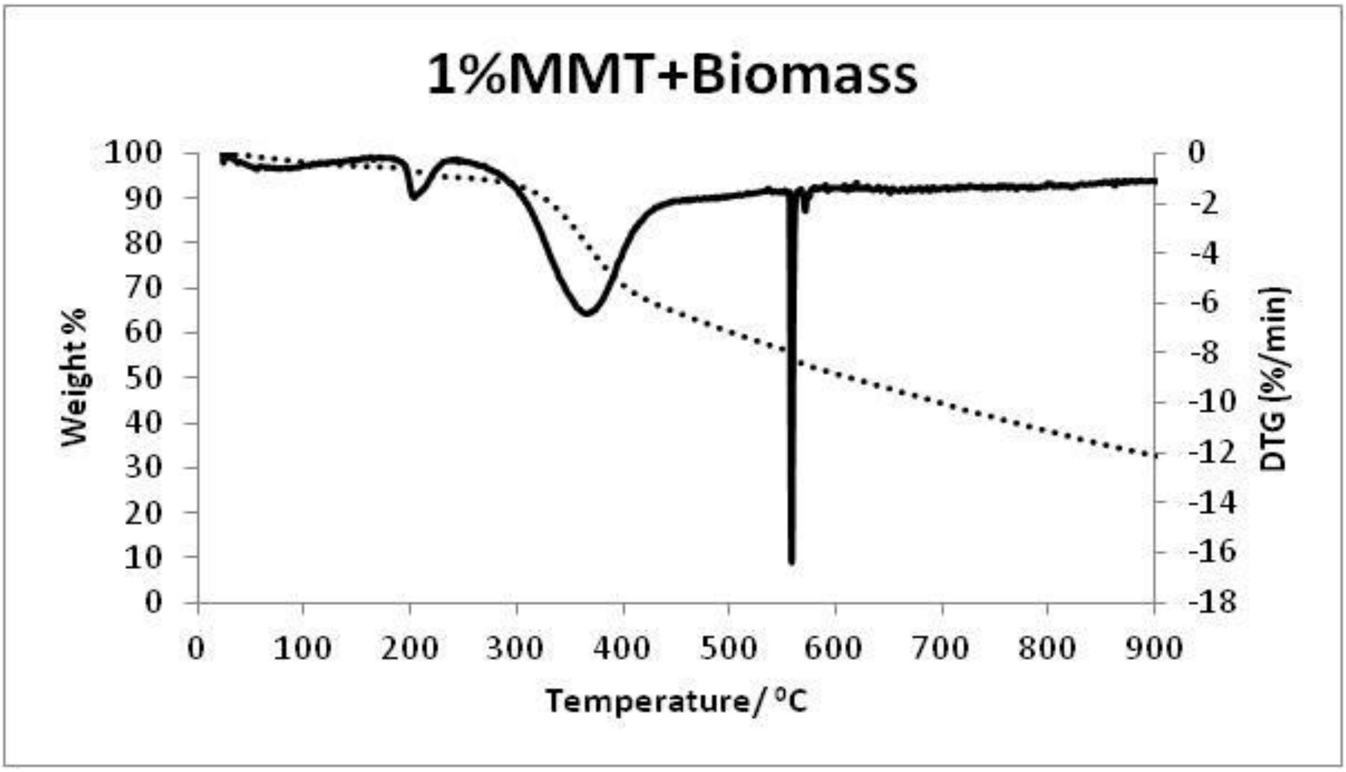

Figure 5.13: DTG plot 1% MMT composited with biomass

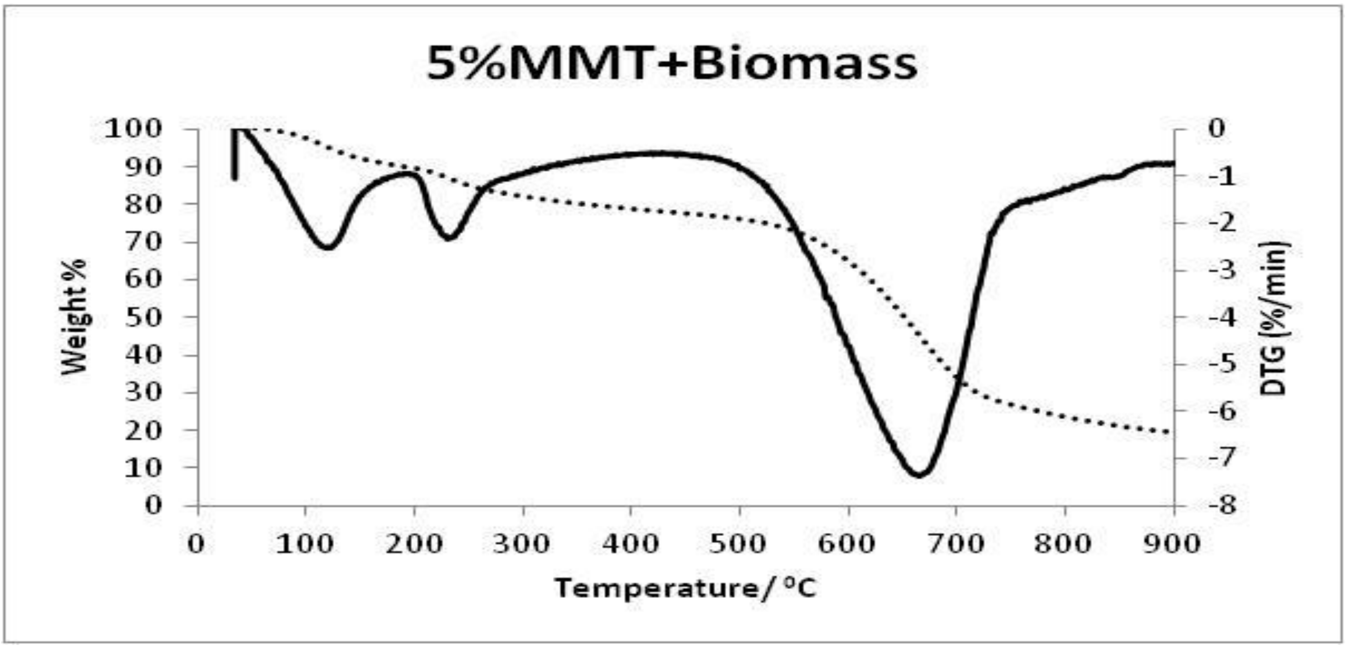

Figure 5.14: DTG plot 5% MMT composited with biomass

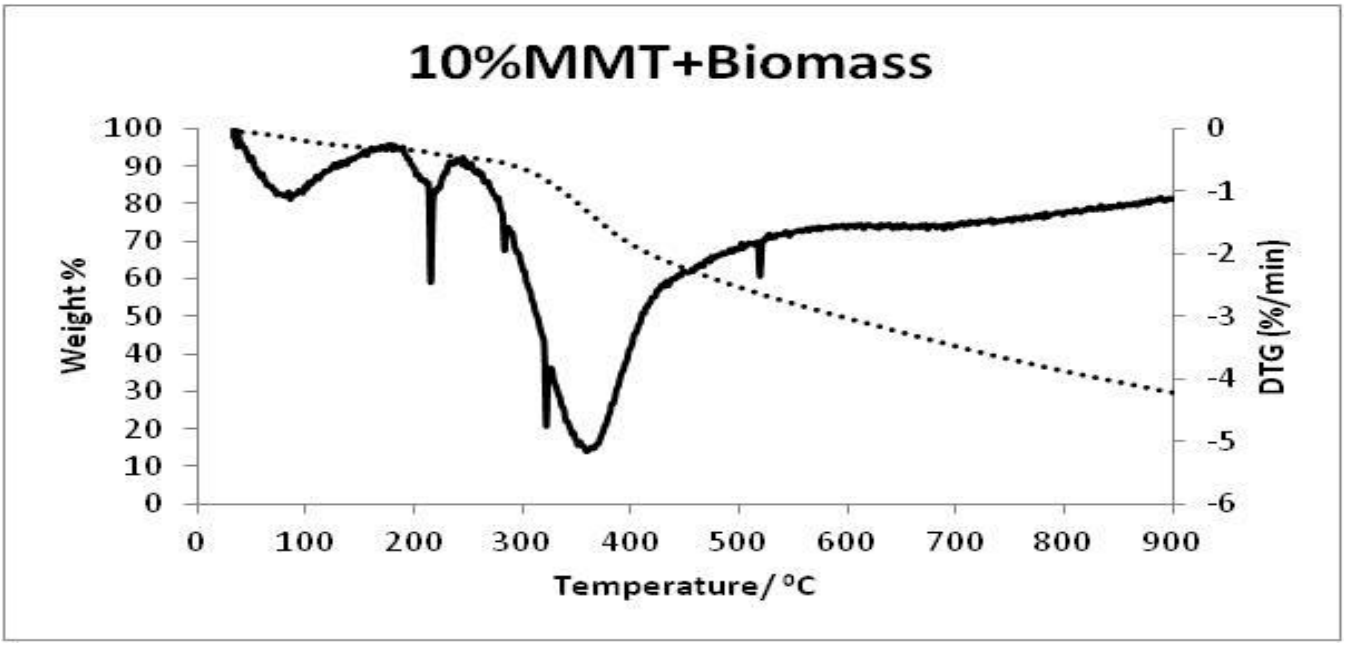

Figure 5.15: DTG plot 10% MMT composited with biomass

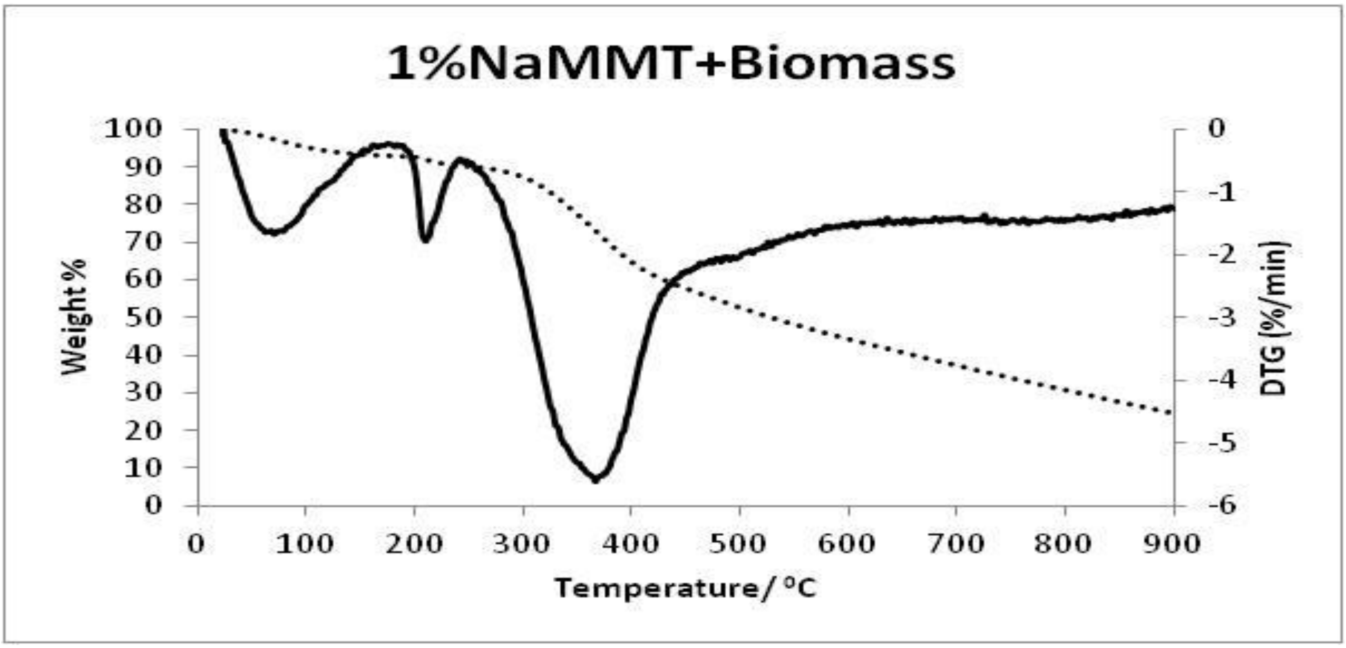

Figure 5.16: DTG plot 1% Na-MMT composited with biomass

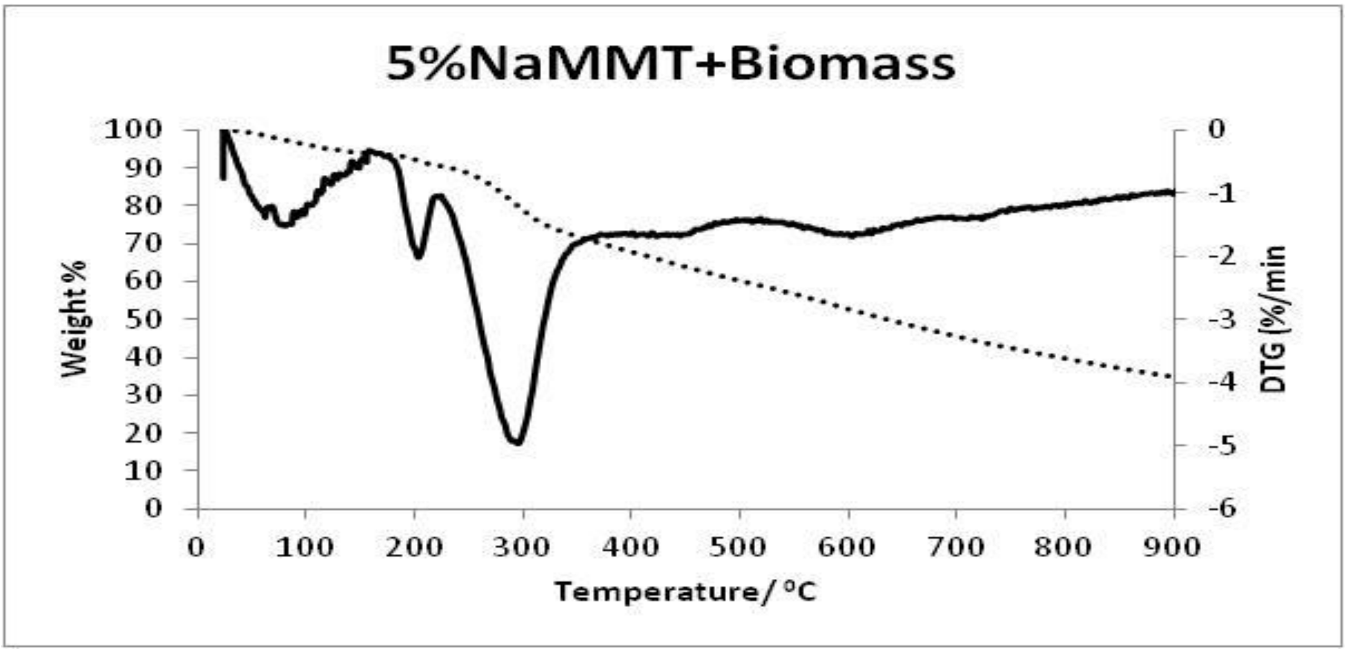

Figure 5.17: DTG plot 5% Na-MMT composited with biomass

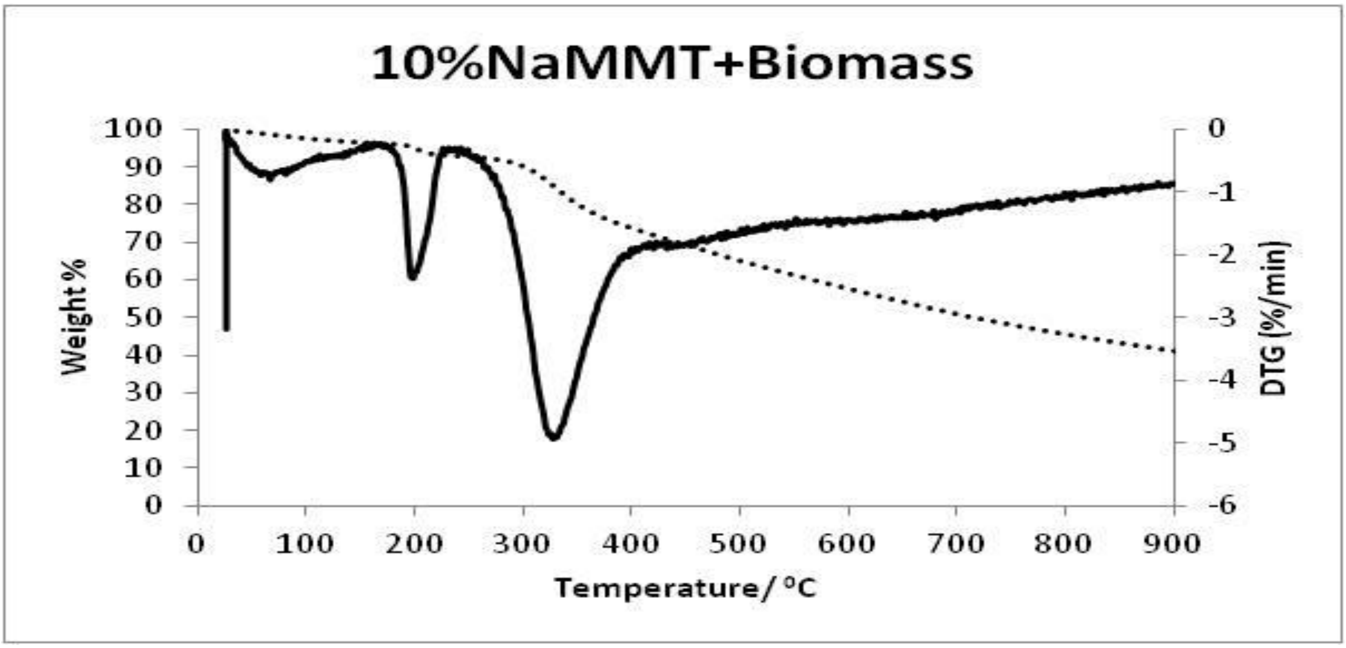

Figure 5.18: DTG plot 10% Na-MMT composited with biomass

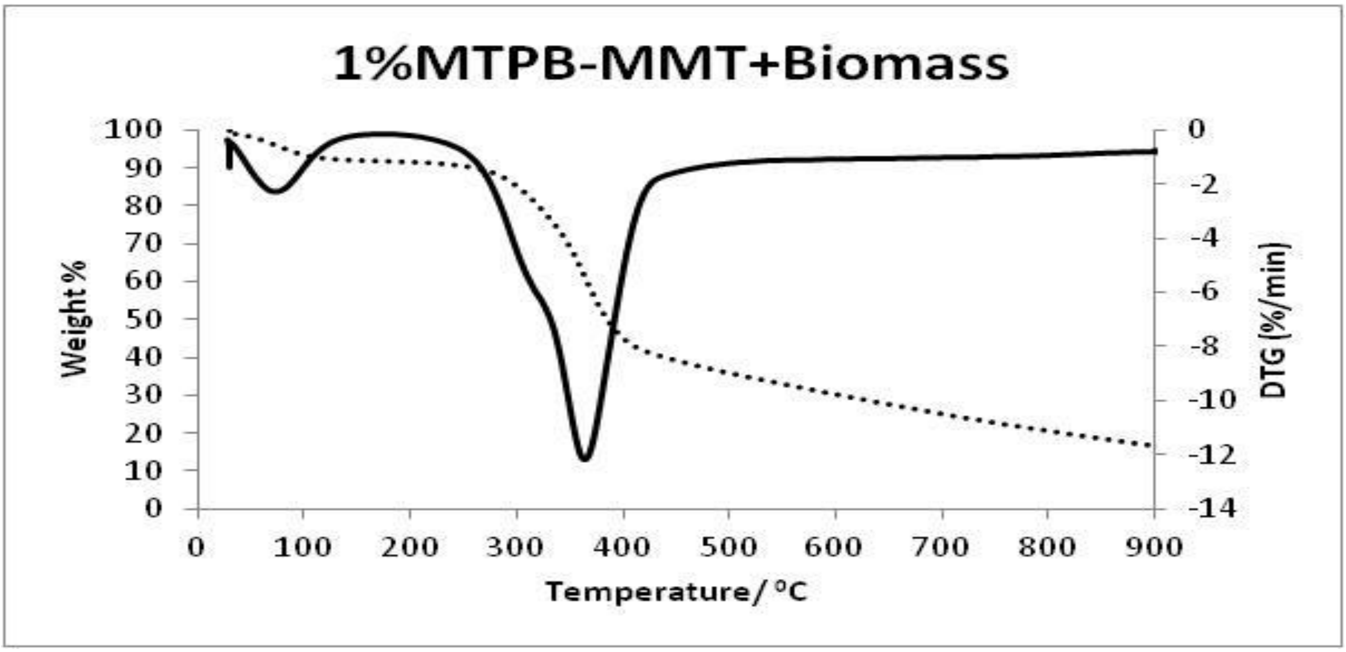

Figure 5.19: DTG plot 1% MTPB-MMT composited with biomass

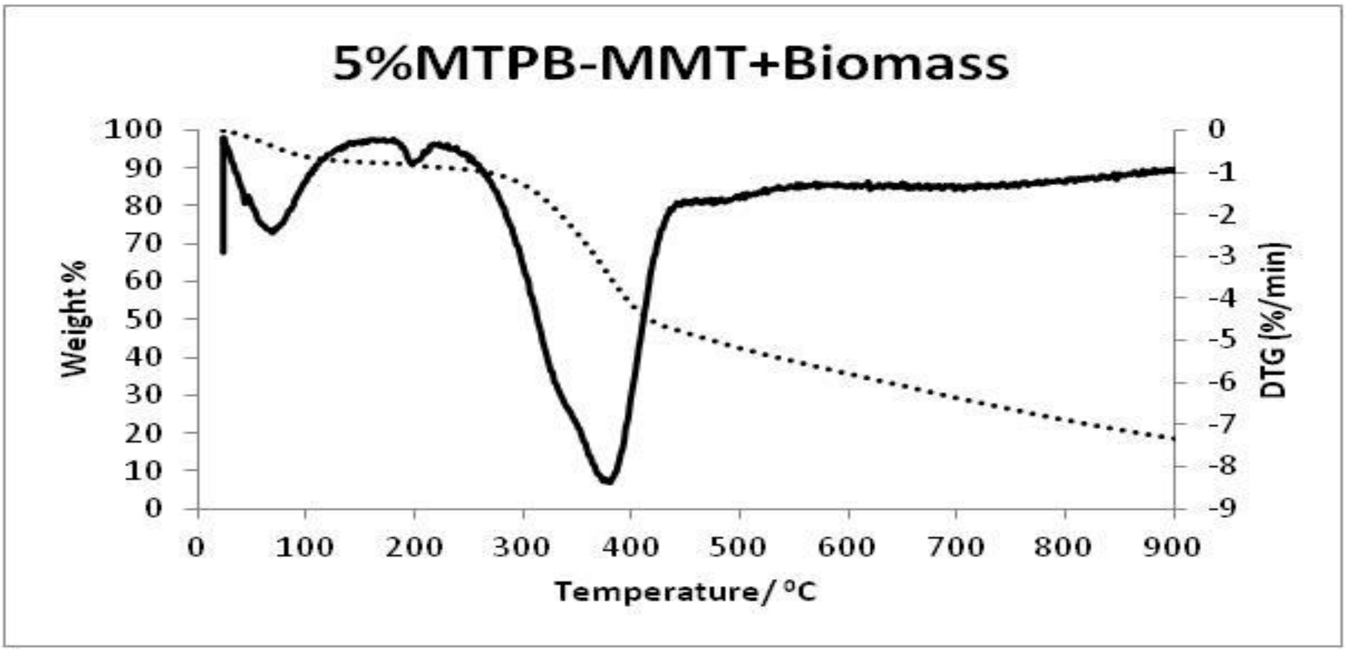

Figure 5.20: DTG plot 5% MTPB-MMT composited with biomass

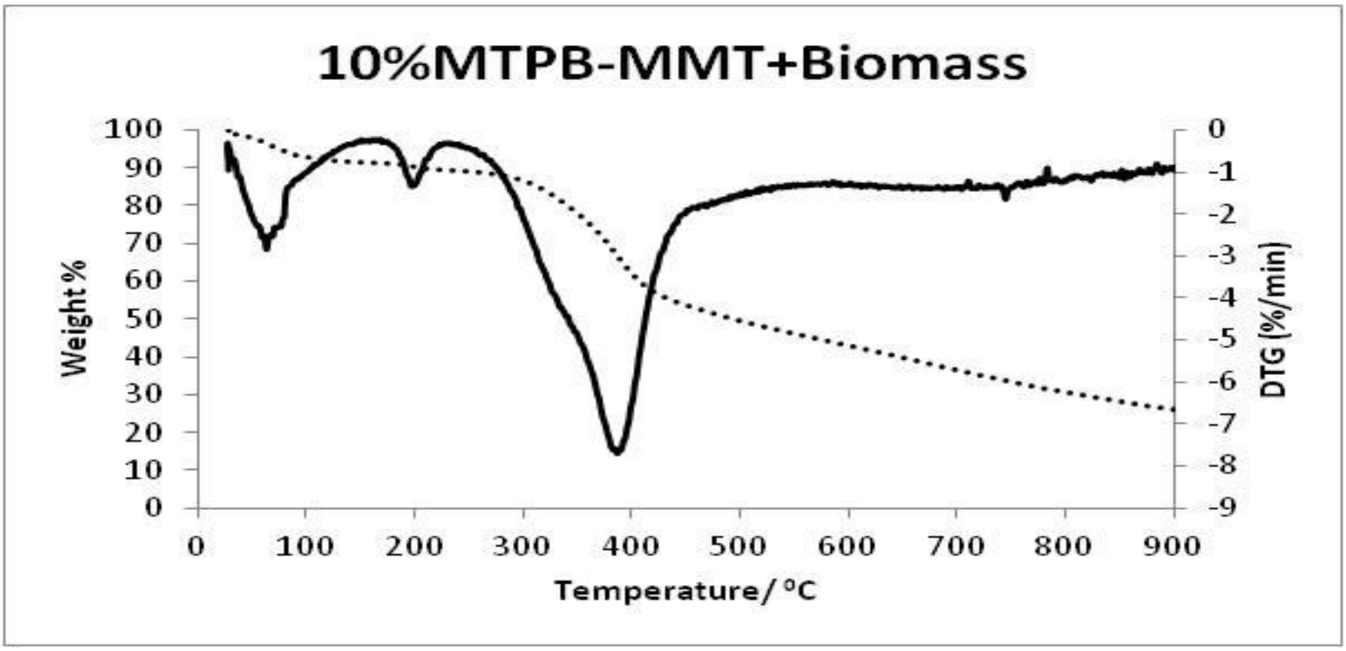

Figure 5.21: DTG plot 10% MTPB-MMT composited with biomass

5.2 Calorific values and flammability

Table 5.2 below shows the classification used to describe flammability. If a material is classified as V-0, it is regarded as non-flammable and self-extinguishing, while V-2 materials are regarded as flammable.

Table 5.2: Classification of combustible materials

Classification	V-0	V-1	V-2
Total flaming combustion time for each specimen (s)	≤10 s	≤30 s	≥30 s
Total flaming combustion time for 3 specimens (s)	≤30 s	≤90 s	≥90 s
Flaming and glowing combustion time for each specimen after second flame application (s)	≤30 s	≤60 s	≥60 s

A fixed amount of each material was subjected to a flame for a period of 5 seconds before the flame source was removed. The total time taken for the material to combust with a noticeable flame from the moment of flame source removal was noted, up to the time it stopped glowing. All the materials were found to be flammable, although the time they showed to combust with and without a flame were different.

Table 5.3: Flammability of the various samples and their classifications

	Total flame and combustion time for each specimen (s)	**Flaming time (s)**	**Glowing time with no flame (s)**	**Classification**	**Calorific Value/MJ**
Sawdust	31	11	20	V-2	17.87
1%MMT+Biomass	33	5	28	V-2	14.49
5%MMT+Biomass	32	5	27	V-2	14.20
10%MMT+Biomass	34	4	30	V-2	13.90
1%NaMMT+Biomass	37	8	29	V-2	14.87
5%NaMMT+Biomass	35	7	28	V-2	12.80
10%NaMMT+Biomass	35	8	27	V-2	12.98
1%MTPB-MMT+Biomass	38	4	34	V-2	17.39
5%MTPB-MMT+Biomass	39	5	34	V-2	15.97
10%MTPB-MMT+Biomass	37	4	33	V-2	15.16
MTPB+Biomass	33	6	27	V-2	13.77

There was a significant elongation of the time the modified materials took to get extinguished when compared to unmodified sawdust. Sawdust burnt with a noticeable flame for a longer time when compared to the modified materials. The modified, materials, however burnt with a glow for a longer time when compared to unmodified sawdust. Overall, the modified materials burnt for longer time when compared to unmodified sawdust.

Unmodified sawdust showed the highest calorific value when compared to the modified materials. Sawdust modified with organoclay showed a caloric value closer to unmodified sawdust when compared to all the other modified materials.

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CHAPTER 6

6. Conclusion and recommendations

6.1 Conclusion

The objectives of the study were largely met. Montmorillonite was purified and successfully converted to sodium-montmorillonite by ion-exchanging the various inorganic cations found in the interlayer space of the clay, using an aqueous sodium chloride solution. Organoclay was prepared using methyl triphenyl phosphonium bromide (MTPB) as the surfactant by the use of the solution blending technique. Composites were prepared with biomass and a) unmodified MMT, b) NaMMT and c) organoclay. For each type of the samples the clay loadings were 1%, 5% and 10%.

The IR spectrum of the nanocomposites showed functional groups which confirmed the incorporation of clay in the wood matrix.

The modification of clay to organoclay increased the interlayer space of the clay as shown by X-Ray Diffraction patterns. This is consistent with the fact that the organic surfactant is bulky when compared to the inorganic cations that it replaced. As expected the 2 theta value was lowered as the intensity increased. This was attributed to the fact that exfoliation took place to a significant extent. The wood dust sufficiently displaced the clay layers leading to exfoliation rather than intercalation of clay. Since the intensity was not zero, this meant that exfoliation was not complete. However, when unmodified montmorillonite was compounded with sawdust, there was almost complete exfoliation as interpreted from the absence of a peak in the lower 2 theta angle in Figure 4.6. This phenomenon was also observed when the biomass was compounded with mono-ionic montmorillonite

The biomass, which was modified with organoclay produced the least amount of residue as shown by thermogravimetric analysis when compared to the those modified with montmorillonite and mono-ionic montmorillonite. The composite which had a 1% loading of organocaly (1% MTPB-MMT+ Biomass) had the longest burning and glowing time and at 17.39 MJ/kg it had a calorific value closest to that of sawdust. This showed that the modification resulted in a material which burns longer than sawdust, without a significantly huge decrease in the calorific value. Of all the modified materials it also had the lowest amount of residue found from the TGA analysis. Since the main aim was to produce a material which burnt for a longer time than usual, it can be said that the major aim of the study was achieved.

6.2 Recommendations

By modifying sawdust with a 1% loading of montmorillonite clay, which in itself has been modified with methyl triphenyl phosphonium bromide, can increase the time that sawdust burns without significantly reducing the calorific value. It is recommended that the practical feasibility of using this composite as fuel for heating and cooking be studied. Pelleting this modified sawdust can result in an even more efficient fuel which burns longer, has more energy per unit volume when compared to other types of biomass fuels like logs, takes up less storage space, easier to store and transport. The pellets made from this material can be used to fire pellet, stoves which can be used in domestic units or even to fire boilers in commercial establishments. The rural districts of Nkonkobe and Amathole in the Eastern Cape province of South Africa can benefit from the local sawmill of Melanie. Instead of burning the sawdust produced there on-site, it can be harnessed to provide useful energy for the surrounding community who are not connected to the national power grid. A compositing and pelleting project can also create the much needed employment for the local people.